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80

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CONTENTS

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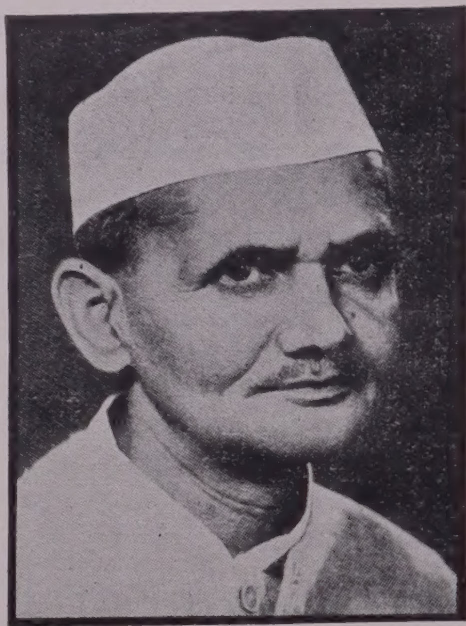

SHRI LAL BAHADUR SHASTRI

In the sad sudden passing away of Shri Lal Bahadur Shastri, Prime Minister, in the early hours of January 11 at Tashkent, India lost one of her noblest sons.

Born in October 1904 near Varanasi (U.P.), Lal Bahadur Shastri joined the Non-cooperation Movement in 1921. After release from jail, he continued his studies in Kashi Vidyapith, and in 1926 joined the Servants of the People's Society as a life member. Later he settled down in Allahabad to pursue his political activities. He took an active part in the local municipal board and in 1930 became the secretary and then president of the District Congress Committee. He was subsequently appointed Secretary of the Provincial Congress Committee.

Shri Shastri became Secretary to Congress Parliamentary Party, U.P. in 1945 and in the next year became Parliamentary Secretary to the Chief Minister. In 1947 he was appointed Minister in Charge of Home Affairs and Transport, U.P. In 1951 he was called upon to act as General Secretary of the Indian National Congress. In 1952 he was appointed Union Minister-in-Charge of Railways and Transportation and became Union Minister of Home Affairs in 1962.

Shri Shastri was unanimously elected Prime Minister of India in May 1964 after the demise of Shri Jawaharlal Nehru. He was the President of the Council of Scientific and Industrial Research and the Chairman of the Atomic Energy Commission and the Planning Commission.

Shri Shastri was a great believer in science. His interest in harnessing scientific knowledge and talent for the maximum benefit of the country was so great that he took all opportunities to place before the scientists the specific needs of the country capable of being tackled by scientific investigations and approach. His slogan of self-reliance and self-sufficiency bestowed a greater sense of responsibility on science and scientific research in the country. In the field of agriculture, he laid stress on scientific method of cultivation.

Hydrodesulphurization of Petroleum Feedstock Part II—Kinetic Study on Hydrotreatment of Heptane Solution of Thiophene

By

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Thiophene in heptane solution has been hydrogenated in vapour phase over cobalt-molybdate catalyst in a bench scale unit. Temperature, heptane and hydrogen feed rates have been varied under atmospheric pressure. A satisfactory kinetic expression has been derived and verified by experimental data. Allowable space velocities for 99 per cent conversion of thiophene into hydrogen sulphide have been predicted and compared with those for conversion of carbon disulphide and dibenzothiophene. The velocity coefficients and energy of activations for hydrogenation of three different organic sulphur compounds have also been compared.

troduction

Different types of organic sulphur compounds like rbon disulphide, carbon oxysulphide, mercaptans, iophenes[1] etc. are present in petroleum feedstocks. these sulphur compounds, thiophenic sulphur is e most resistant to removal by hydrotreatment[2]. a previous publication[3] the kinetic study on hydro-atment of heptane solution of carbon disulphide ve been dealt with. This paper is concerned with the idy on hydrodesulphurisation of heptane solution thiophene.

eory

The theoretical kinetic expression for hydro-sulphurisation of organic sulphur compounds has en already derived[3] and the same is reproduced here

$$-\frac{F}{W_R} \ln \frac{x_{s2}}{x_{s1}} = k_H e^{-E/RT} x_H^m P \qquad \ldots\ldots\ldots(1)$$

perimental

Apparatus: The bench scale unit consists of equip-ents already used in our previous study on hydro-eatment of heptane solution of carbon disulphide[3]. aterials used are the same as given in Part I of this ries.

Procedure: The charge of catalyst, already used in process, was the same as in our previous study[3]. It was kept inside the reactor tube. The operational procedure was the same as before, but since the catalysts used in the present case were in a sulphided state from the very initial stage about ten hours were found to be sufficient for catalyst activity to reach an equilibrium value. Experimental data were collected after the activity of the catalyst reached a steady equilibrium value under any experimental condition.

Estimation of Sulphur: The quantitative estimation of thiophene was done colorimetrically with isatin ferric chloride solution, and hydrogen sulphide in noncondensable gas was estimated by absorbing it in cadmium acetate solution followed by iodometric titration.

Results

Experimental data presented in Table 1 show the percentage conversion of thiophenic sulphur into hydrogen sulphide at different flow rates and temperatures. 50 g. of cobalt molybdate catalyst, already sulphided during the hydrogenation of carbon disulphide[3], were used. Since the present set of experi-

TABLE 1

Expt. No.	W_R, *g.* *Catalyst used*	F_H *g. moles* H_2 *per hour in feed*	F_{HC}, *g. moles heptane per hour in feed*	*F, total feed, g. moles per hour*	*Temp °C*	*Thiophene in heptane feed, ppm wt/wt*	*Thiophene in heptane product, ppm wt/wt*	*Per cent conversion of Thiophene into* H_2S
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	50	0.177	1.224	1.401	333	1480	1260	14.95
2	,,	0.107	1.200	1.307	333	1480	1390	6.10
3	,,	0.282	1.158	1.440	332	1480	1222	17.35
4	,,	0.470	2.220	2.690	329	1470	1360	7.55
5	,,	0.312	2.034	2.346	329	1470	1390	5.66
6	,,	0.368	2.028	2.396	329	1470	1307	11.32
7	,,	0.423	1.956	2.379	329	1470	1280	13.20
8	,,	0.410	2.184	2.594	330	1390	1250	10.00
9	,,	0.892	1.860	2.752	330	1470	1220	17.00
10	,,	0.161	1.968	2.129	326	1470	1390	5.66
11	,,	0.738	1.278	2.016	328	1470	1190	18.90
12	,,	0.773	1.212	1.985	330	1470	1220	17.00
13	,,	0.460	1.170	1.630	331	1470	1220	17.00
14	,,	0.698	1.248	1.946	332	1470	1190	18.90
15	,,	0.282	1.128	1.410	327	1470	1220	17.00
16	,,	0.089	0.588	0.677	327	1487	1268	14.05
17	,,	0.548	0.630	1.178	353	1487	1182	20.50
18	,,	0.594	0.642	1.236	379	1530	1142	25.30
19	,,	0.525	0.696	1.221	404	1530	1112	27.30
20	,,	0.485	0.672	1.157	428	1530	1057	31.00
21	,,	0.473	0.570	1.043	272	1530	1196	21.80
22	,,	0.631	1.140	1.771	328	1530	1180	22.75
23	,,	0.658	1.098	1.756	354	1530	1168	23.65
24	,,	0.664	1.188	1.852	380	1530	1168	23.65
25	,,	0.650	1.140	1.790	405	1530	1127	26.35
26	,,	0.695	1.080	1.775	428	1530	1098	28.20
27	,,	0.566	0.564	1.130	273	1530	1224	20.00
28	,,	0.627	0.588	1.215	275	1500	1194	20.40
29	,,	0.562	0.552	1.114	380	1500	1153	23.10
30	,,	0.580	1.212	1.792	455	1500	1050	30.10
31	,,	0.510	1.152	1.662	376	1500	1060	29.40
32	,,	0.485	0.426	0.911	269	1500	1195	20.35
33	,,	0.477	0.510	0.987	272	1500	1180	21.30
34	,,	0.745	3.012	3.757	328	1500	1376	8.33
35	,,	0.506	0.139	0.645	328	1500	139	90.70
36	,,	0.220	0.570	0.790	329	1500	1167	22.20
37	,,	0.196	0.139	0.335	328	1500	248	83.50
38	,,	0.396	0.240	0.636	329	1500	139	90.70
39	,,	0.527	1.440	1.967	325	7200	6270	12.97
40	,,	0.567	1.494	2.061	328	3545	2962	16.45
41	,,	0.535	1.494	2.029	329	1695	1335	21.30
42	,,	0.238	0.107	0.345	325	5350	1280	76.10
43	,,	0.315	0.091	0.406	325	5350	1225	79.70
44	,,	0.396	0.120	0.516	325	5350	1390	77.10
45	,,	0.487	0.269	0.756	325	5350	1390	74.00

TABLE 2

Expt. No. (1)	x_H, *molefraction of Hydrogen* (2)	$x_{S1} \times 10^4$, *molefraction Thiophene in feed* (3)	$x_{S2} \times 10^4$ *molefraction Thiophene in product* (4)	$[-F/W_R \ln x_{S2}/x_{S1}] \times 10^3$ *g. moles/(hr.) (g. catalyst)* (5)	$10^3/T$ °K^{-1} (6)	$\ln[-F/W_R \ln x_{S2}/x_{S1}/x_H]$ *g. moles/(hr) (g. catalyst (molefraction H_2)* (7)
1	0.126	15.4	13.2	4.50	1.65	-3.32
2	0.090	16.0	15.0	1.62	1.65	-4.00
3	0.196	14.1	11.8	5.43	1.65	-3.57
4	0.175	14.4	13.3	4.20	1.60	-3.72
5	0.133	15.1	14.1	2.67	1.66	-3.90
6	0.204	13.9	12.3	5.72	1.66	-3.56
7	0.178	14.4	12.5	6.77	1.66	-3.26
8	0.158	13.9	12.5	5.47	1.66	-3.36
9	0.324	11.8	9.8	10.15	1.66	-3.45
10	0.076	16.2	15.2	2.52	1.67	-3.40
11	0.367	11.1	9.0	9.25	1.66	-3.68
12	0.389	10.8	8.9	7.30	1.66	-3.97
13	0.282	12.6	10.4	6.06	1.66	-3.84
14	0.359	11.2	9.1	8.14	1.66	-3.77
15	0.200	14.0	11.6	5.25	1.67	-3.64
16	0.131	15.4	13.2	2.05	1.67	-4.15
17	0.465	9.5	7.6	3.99	1.60	-4.74
18	0.481	9.5	7.1	7.26	1.54	-4.18
19	0.431	10.4	7.5	7.75	1.48	-4.00
20	0.419	10.6	7.3	8.60	1.43	-3.88
21	0.454	10.0	7.8	5.15	1.84	-4.47
22	0.356	11.7	9.1	8.96	1.67	-3.68
23	0.375	11.4	8.7	9.50	1.60	-3.66
24	0.358	11.7	8.9	10.00	1.53	-3.56
25	0.364	11.6	8.5	9.63	1.48	-3.62
26	0.391	11.1	8.0	11.78	1.43	-3.49
27	0.500	9.1	7.3	4.02	1.84	-4.80
28	0.516	8.7	6.9	4.59	1.83	-4.71
29	0.503	8.9	6.8	5.90	1.53	-4.43
30	0.324	12.1	8.5	12.80	1.37	-3.22
31	0.307	12.4	8.8	11.80	1.53	-3.26
32	0.533	8.3	6.6	3.37	1.85	-5.05
33	0.483	9.2	7.2	4.76	1.84	-4.61
34	0.199	14.3	13.1	6.49	1.67	-3.42
35	0.785	3.84	0.36	30.90	1.67	-3.23
36	0.279	12.90	10.00	5.22	1.67	-4.00
37	0.585	7.74	1.28	12.10	1.67	-3.87
38	0.620	6.80	.63	30.10	1.66	-3.02
39	0.268	62.80	54.60	5.44	1.67	-3.89
40	0.275	30.60	25.60	7.30	1.670	-3.62
41	0.264	14.90	11.70	9.74	1.665	-3.30
42	0.690	19.75	4.72	9.86	1.67	-4.37
43	0.780	14.00	2.84	12.85	1.67	-4.10
44	0.717	18.70	2.73	15.20	1.67	-3.84
45	0.643	22.80	5.92	20.30	1.67	-3.45

ments were carried out under atmospheric pressure equation (1) may be expressed as

$$-\frac{F}{W_R}\ \ln\ \frac{x_{s2}}{x_{s1}} = k_H e^{-E/RT}\ x_H{}^m \ldots\ldots(2)$$

From an analysis of the experimental data by the same procedure (Figs 1 & 2) as adopted in Part I[3] the values of m, E and k_H were found to be 1.0, 4170 g. cal /g. mol and 0.55 g. mol/(hr) (g. catalyst) (molefraction H_2). Hence the experimental data may be correlated with the following expression.

$$-\frac{F}{W_R}\ \ln\ \frac{x_{s2}}{x_{s1}} = 0.55\ e^{-2100/T}\ x_H \qquad \ldots.(3)$$

Table 2 represents the values of the functions plotted in Figs. 1 and 2.

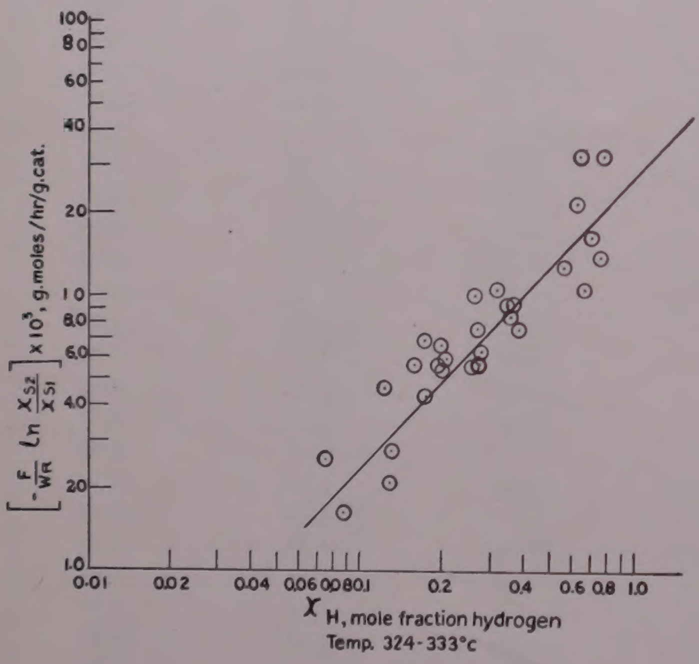


Fig. 1.

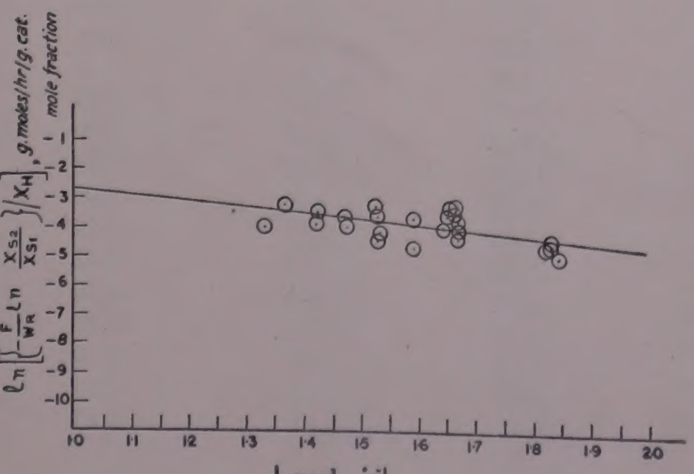
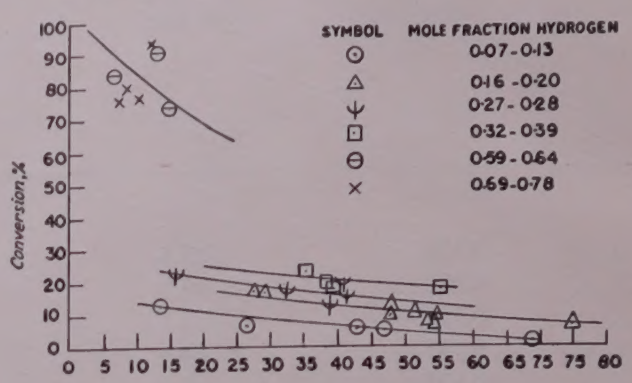


Fig. 2.

Effect of Space Velocity on Per Cent Conversion: The effect of space velocity, expressed as g.moles feed (Hydrogen+Heptane)/(hr) (g. catalyst) on per cent conversion of thiophenic sulphur into hydrogen-sulphide is shown in Fig. 3.



$F/W_R \times 10^3$, g.moles/(hr) (g.catalyst)
Temp. 324 – 333°C

Fig. 3.

Discussion

For naphtha steam-reforming process, organic sulphur content in hydrocarbon feedstock is to be reduced to 5-8 ppm[2]. Thiophenic sulphur is the most resistant to removal by hydrotreatment. In the present study, it may be found from Fig. 2 that under atmospheric pressure the allowable space valocity for 99 per cent conversion of thiophenic sulphur into hydrogen sulphide at 350°C and 0.5 atmosphere of hydrogen partial pressure is 2.06×10^{-3} g. moles (Hydrogen+Heptane)/(hr) (g.catalyst). From Fig. 1 it is found that the space velocity, $\frac{F}{W_R}$ is directly proportional to partial pressure of hydrogen between the range of 0.07-0.8 atm. of hydrogen partial pressure. Assuming that this finding is applicable up to 10 atm. of hydrogen partial pressure, the allowable space velocity for 99 per cent conversion of thiophenic sulphur at 0.5 mole fraction of hydrogen and 350°C may be estimated as 4.12×10^{-2} g. mol. (Hydrogen+Heptane)/(hr) (g. catalyst).

Comparing the kinetic expression (equation 3) with that presented in our previous paper[3] (equation 8), it is found that for same per cent conversion under 350°C and same partial pressure and mole fraction of hydrogen space velocity, $\frac{F}{W_R}$ for thiophenic sulphur removal is about 5.67 times lesser than that for sulphur removal from carbon disulphide. It has been shown[3] that for hydrogenation of dibenzothiophene in naphtha solution[4] the space velocity for same per cent con-

version under similar conditions is about 7.83 times less than that for sulphur removal from carbon disulphide. This might be expected because of the higher molecular weight of dibenzothiophene.

The values of the velocity coefficient, k_H, and energy of activation, E, for hydrogenation of three different organic sulphur compounds may be compared from Table 3.

TABLE 3

System	k_H, *g. moles/(hr) (g. catalyst) (mole fraction* H_2)	E, *g. cal / g. mol*
1. Hydrogenation of CS_2 in heptane solution (Ghosal et-al).[3]	0.532	2000
2. Hydrogenation of thiophene in heptane solution (Present work).	0.550	4170
3. Hydrogenation of dibenzo-thiophene in naphtha solution (From Wilson & Voreck's work on the assumption that space velocity, F/W_R is directly proportional to partial pressure of hydrogen up to 10 atm of hydrogen pressure).	0.290	3800

Nomenclature

- e = constant, 2.72
- E = energy of activation, g. calories/g. mol
- F = total feed, g. moles (hydrogen+hydrocarbon) per hr
- F_H = g. moles hydrogen/hr
- F_{HC} = g. moles hydrocarbon/hr
- k_H = velocity coefficient, g. moles/(hr) (g. catalyst) (mole fraction H_2)
- m = exponent on partial pressure of hydrogen
- P = total pressure, atm
- P_H = partial pressure of hydrogen, atm
- P_S = partial pressure of sulphur compounds, atm.
- R = gas constant, 1.987 g. cal/(g. mol) (°K)
- T = absolute temperature, °K
- V_H = velocity of hydrogenation of organic sulphur compounds, g. moles/(hr) (g. catalyst)
- W_R = weight of catalyst, gms.
- x_H = mole fraction of hydrogen
- x_S = mole fraction of sulphur compound
- x_{S1} = mole fraction of sulphur compound at inlet to the catalyst bed
- x_{S2} = mole fraction of sulphur compound at outlet from the catalyst bed

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The authors acknowledge the valuable assistance rendered by Shri K. P. Rao during the preparation of the catalyst and that by Shri D. Roy during the experimental set-up and initial start-up of the experiments. Their thanks are also due to Dr. K. R. Chakravorty, General Manager, for his active interest in the work. Shri Tinkari Banerjee, Operator, assisted the authors throughout the experimental part of this work.

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Effect of Phosphate Ions on the Adsorption and Exchange of NH_4^+ Ions by Soils

By

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There is a greater adsorption of NH_4^+ ions by soils when ammonium fertilizers are added in the form of ammonium phosphates, thus showing a measurable effect of phosphate ions on the adsorption and exchange of NH_4^+ ions by soils. Comparing mono-ammonium and diammonium phosphates, it has been found that the latter results in a greater amount of adsorption and recovery of NH_4^+ ions. Amroati black soil, containing predominantly a montmorillonitic type of clay mineral, showed the maximum amount of adsorption and recovery of NH_4^+ ions as compared to other soils.

With addition of ammonium fertilizers to soil, NH_4^+ ions are held by soil in a free, exchangeable and fixed form. Of these, usually exchangeable ammonium is available to plants, either directly or through nitrification, while the free form is likely to be lost through leaching and only a small portion of fixed ammonium is supposed to be accessible to nitrifying bacteria. The adsorption and exchange of NH_4^+ ions by the soil depends chiefly on the nature and amount of clay mineral present, cation-exchange capacity, texture, organic matter and pH of the soil. It also depends on the composition of fertilizers used[1]. Not much information is available in regard to the effect of phosphate ions on the adsorption and recovery of NH_4^+ ions especially in case of Indian soils. A study was, therefore, undertaken to notice this effect on three different Indian soils, when treated with ammonium fertilizers bearing phosphate ions, viz. mono-ammonium and di-ammonium phosphates.

Experimental

Materials: The representative surface soil samples used in this study were Dinhata (W. Bengal) alluvial silty loam, Amroati (Maharashtra) black loam, and Sindri (Bihar) red sandy clay loam. Their main characteristics are given in Table 1.

Method: Ammonium chloride, mono- and di-ammonium phosphate solutions were so prepared that 20 ml. of each contained 10 mg. of NH_4^+ nitrogen. 10 g. of each air-dried soil sample screened through 2 mm. sieve (B.S.S.) were treated with 20 ml. of the above prepared ammonium chloride, mono- and di-ammonium phosphate solutions respectively. The soil suspension in each case was made to 100 ml. by adding distilled water, shaken for 12 hours kept overnight and filtered. An aliquot was taken from the filtrate; and its ammonium content was estimated by distillation with magnesium-oxide and ammonia absorbed in an excess acid[2]. The ammonia saturated soils were washed with 35 per cent alcohol to remove the free ammonium. Exchangeable ammonium was determined by leaching the washed soil with (N) KC1 solution. The pH of the soil suspension, after addition of ammonium fertilizer solutions, was determined with a Cambridge glass electrode pH meter. The pH of the soil suspension containing 10 g. of soil and 100 ml. of water were also determined under identical conditions.

Results & Discussion

From Table 2, it is seen that there is more adsorption of NH_4^+ from mono-ammonium phosphate and diammonium phosphate than from ammonium chloride by the three soils. Greater amounts of NH_4^+ ions taken up from ammonium phosphates than from ammonium chloride may be due to the fact that cations replaced by NH_4^+ are precipitated as insoluble phosphate and thus influencing the equilibrium[3]. When comparing the two ammonium phosphate sources, the adsorption of NH_4^+ ions from diammonium phosphate is greater

TABLE 1—CHARACTERISTICS OF VARIOUS SOILS USED

Soil Type	*Clay Minerals Present*	*Sand, %*	*Silt, %*	*Clay, %*	*C.E.C., m.e./100 g.*
Dinhata alluvial silty loam	Illite mainly. Kaolinite and Montmorillonite are also present.	22	57	14	4.70
Amroati black loam	Montmorillonite mainly.	31	22	27	52.90
Sindri red sandy clay loam	Illite mainly. Kaolinite and Montmorillonite are also present.	58	5	29	12.60

TABLE 2—AMOUNT OF NH_4^+ NITROGEN ADSORBED BY VARIOUS SOILS

(Treated at the rate of 10 mg of NH_4^+ Nitrogen per 10g. of Soil)

Soil Type	*Initial pH of Soil Suspension (soil: water. 1:10)*	*Mono-ammonium Phosphate*		*Di-ammonium Phosphate*		*Ammonium Chloride*	
		pH of Soil Suspension	*Ammonium Nitrogen Adsorbed, mg.*	*pH of the Soil Suspension*	*Ammonium Nitrogen Adsorbed, mg.*	*pH of the Soil Suspension*	*Ammonium Nitrogen Adsorbed, mg.*
Dinhata alluvial silty loam	6.60	5.90	2.13	7.30	4.26	6.10	0.78
Amroati black loam	8.70	7.00	7.58	8.05	8.34	8.05	6.57
Sindri red sandy clay loam	6.45	5.60	4.04	7.40	5.54	5.75	3.78

TABLE 3—AMOUNT OF EXCHANGEABLE NH_4^+ NITROGEN AND PERCENTAGE OF NH_4^+ NITROGEN RECOVERY FROM VARIOUS SOILS
(Treated at the rate of 10 mg. of NH_4^+ Nitrogen per 10g. of Soil)

Soil Type	*Mono-Amm. Phosphate*		*Di-amm. Phosphate*		*Ammonium Chloride*	
	Exchangeable, mg.	*Percentage of Recovery from Adsorbed*	*Exchangeable, mg.*	*Percentage of Recovery from Adsorbed*	*Exchangeable, mg.*	*Percentage of Recovery from Adsorbed*
Dinhata alluvial silty loam	0.70	32.86	1.68	39.43	0.50	64.10
Amroati black loam	6.04	79.98	5.97	71.58	5.52	84.02
Sindri red sandy clay loam	2.61	64.62	3.28	59.21	2.53	66.93

than from mono-ammoium phosphate. With the addition of mono-ammonium phosphate to the soils, the pH of the system decreases in each soil, while with the addition of diammonium phosphate the pH of Dinhata soil has increased from 6.60 to 7.30, of Sindri red soil from 6.45 to 7.40, but in case of Amroati black soil the pH changed from 8.70 to 8.05. Many workers[4,5] have observed that NH_4^+ adsorption is decreased with decrease in pH of the system, and hence may be the cause for low adsorption of NH_4^+ ions from mono-ammonium phosphate as compared to diammonium phosphate.

Further, it is evident from Table 3 that there is a greater amount of exchangeable NH_4^+ nitrogen recovery in case of diammonium phosphate and mono-ammonium phosphate treatments in comparison to ammonium chloride. However, percentage of exchangeable ammonium is maximum in the case of ammonium chloride addition, followed by those by addition of mono- and di-ammonium phosphates (Table 3). Obviously phosphate ions present in mono-ammonium phosphate and diammonium phosphate treatments appears to have facilitated the fixation of NH_4^+ ions[6,7] thus resulting in low percentage recovery as compared to ammonium chloride.

Different soils show variation in power of adsorption and exchange of NH_4^+ ions. This is of the order of Amroati black soil > Sindri red soil > Dinhata soil. These variations may be due to the nature and amount of clay minerals present[8-10]. Amroati black soil contains predominantly montmorillonitic type of clay mineral causing greater adsorption and exchange of NH_4^+, whereas Dinhata soil containing low amount of illitic and kaolinitic type of clay mineral causes low adsorption and exchange of NH_4^+ ions.

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Studies on the Reversion of Polyphosphate in Cooling Water

By

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Studies have been carried out under different conditions on the reversion of sodium polyphosphate in cooling tower waters and also in water samples prepared in the laboratory containing various dissolved salts. Effect of some additives on the rate of reversion has also been studied. Al^{3+} has been found to retard the rate of reversion to a considerable extent.

In cooling waters polyphosphate is used either alone or in combination with chromate to inhibit corrosion of heat exchangers and to prevent formation of scales[1-7]. Indelli[8] reviewed the use of low, medium and high molecular weight sodium polyphosphate as corrosion inhibitor. Bregman[9] et al after studying corrosion of mild steel with polyphosphate (25 mg/1) and a multivalent ion at a concentration of 2 mg/1, has observed that Co, Ce, Cr, Mn, Cd, Zn and Ni had inhibiting action whereas V, Si, Te, Zr, Fe, Cu, Sb, Be and Al increased corrosion. A method has been developed[10] for treating circulating water using a Zinc-alkali metal polyphosphate which provided better scale control than the alkali metal polyphosphate alone. Tseidler[11] treated the cooling water with tri-polyphosphate. In another process[12] water was treated with three constituents to inhibit corrosion, using a water-soluble molecularly dehydrated polyphosphate salt (5-80 ppm), a water-soluble ortho-polyphosphate salt (5-20 ppm) and an organic chelating agent (10-25 ppm). Beecher and Savinelli[13] suggested the use of a zinc-chromate organic surface active agent as inhibitor for controlling corrosion in an open circulating cooling water system.

Chromate-polyphosphate mixture in combination with non-ionic surface active agents[14] of high molecular weight has been found to improve inhibition. Polyphosphate-tannins and sodium-zinc polyphosphate-organic treatments were also found beneficial and of much utility where stream pollution precludes the use of chromate inhibitor. In the so-called dianodic method a dual treatment of molecularly dehydrated phosphate and chromate over a selective pH range is employed. This method produces effective control over pitting and tuberculation. The 'dianodic method' includes phosphate dianodic, zinc dianodic, fluoride dianodic and also combinations of these.

Sodium polyphosphate has a tendency to react with water to form ultimately orthophosphate, which is known as hydration, hydrolysis or reversion. The formation of orthophosphate is undesirable for two reasons; it reduces the amount of polyphosphate ion in water and secondly the introduction of orthophosphate ion in the system may result in the formation of relatively insoluble calcium, magnesium and iron salts which lead to the formation of sludge and scales. Various studies[15-17] have been carried out on the stability of polyphosphate in water. Karbe and Jander[17] found that the stability of sodium trimetaphosphate decreases with the decreasing concentration from 1 to 0.I.N.

Smith[18] studied the significant influence of calcium and magnesium on the rate of reversion of sodium polyphosphate glass due to formation of soluble complexes. Green[19] carried out reversion studies of seven molecularly dehydrated sodium polyphosphate and concluded that rate of reversion was usually unaltered or decreased in the presence of magnesium, while calcium increased the rate of reversion.

Temperature is one of the major factors which influence the rate[20-28] of reversion of sodium polyphosphate. The variation of the rate constant K, with tem-

TABLE 1—REVERSION OF COMMERCIAL SODIUM POLYPHOSPHATE AT DIFFERENT pH AND UNDER VARIOUS CONDITIONS

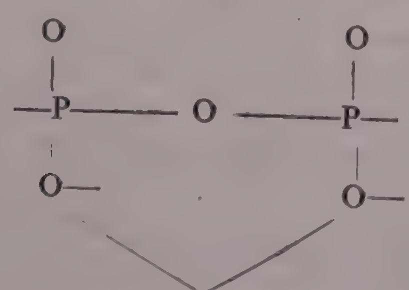
(Temp. 40°C; Initial Concentration of Polyphosphate, 18.6 ppm. as PO_4)

Time, hr.	*NH_4NO_3, 500 ppm.* Reversion, %			*NH_4NO_3 (500 ppm) + NaCl (40 ppm)* Reversion, %			*Synthetic Water* Reversion, %		
	pH 7	*pH 8*	*pH 9*	*pH 6*	*pH 7.0*	*pH 9.0*	*pH 6.0*	*pH 7.0*	*pH 9*
24	16.21	13.51	8.74	16.22	13.51	5.37	34.79	22.04	8.6
48	35.13	26.50	19.50	39.18	33.80	9.19	56.52	46.24	8.6
72	51.29	40.5	26.00	48.64	48.65	12.44	67.39	57.02	8.6
96	66.54	54.0	33.30	64.86	57.84	13.44	78.27	65.05	8.6
120	—	—	—	78.34	72.95	13.44	86.42	73.11	8.6
144	89.17	78.38	38.81	—	—	—	—	—	—
168	94.58	83.78	44.26	82.15	81.10	13.44	89.12	81.20	16.67

perature can be denoted by Arrhenius equation, $K = Ae^{-E/RT}$, where A is the frequency factor, E the activation energy, R and T are respectively the gas constant and absolute temperature.

The hydrolytic degradation of all chain phosphates are strongly catalyzed by hydrogen ion[26]. Various enzymes affect the rate of hydrolysis to a great extent[29]. Colloidal gels, such as the hydrated oxides of iron, cobalt, nickel, aluminium and the rare earths accelerate the hydrolytic degradation of polyphosphates[31].

The machanism[31] of reversion of low molecular weight phosphates is relatively straight forward. Simultaneous scissions of P-O-P linkages in the same molecule ion do not occur and the activated complex is thought to be due to a chelation of water, hydronium ion or hydrated metal ion with a group shown below



or the activated complex may involve the d-orbitals of the phosphorous so that there would be five bonds proceeding from this atom in the activated complex. The present investigation was undertaken to find out suitable additives which could reduce the reversion of polyphosphate in cooling water.

Experimental

Sodium hexametaphosphate (BDH L.R.) and the sodium polyphosphate prepared in laboratory were used in the study on the reversion of polyphosphate. Synthetic sodium polyphosphate was prepared by the classical method[32,33]. Sodium dihydrogen orthophosphate was heated in a platinum dish in a muffle furnace maintained at 700±20°C, and the molten mass thus obtained was chilled by pouring on stainless steel plates placed on ice. The weight average molecular weight (Mw), determined by the viscosity method[33], was found to be 13,000

Samples of water were collected from ammonia synthesis cooling tower in the Sindri plant. The analyses of the water samples have already been given in a previous communication[2]. Water sample prepared in the laboratory contained $CaSo_4$–123 ppm, NH_4NO_3–500 ppm and NaCl–40 ppm. A.R. quality chemicals were used. Sample of santobrite (sodium pentachlorophenate) was obtained from Monsanto Chemicals, USA.

All pH measurements were carried out by means of a Cambridge pH meter (Model L 382894) with glass membrane electrode and calomel as reference electrode.

The polyphosphate in water was determined by the usual colorimetric method[34], while a modified method[35], developed in this laboratory, was used for it in presence of chromate.

Reversion Experiments: Water samples were taken in a litre flask. Polyphosphate with or without chromate was added and the solution made up to one litre. pH of the solutions were adjusted to the desired values. The initial orthophosphate content was determined and then the solutions were taken in 250 ml. polythene bottles kept in a thermostat maintained at 40°±0.1°C.

Known volumes of these samples were taken out at suitable intervals and orthophosphate in them was determined. From the initial and final concentrations of orthophosphate in the water, the degree of reversion was calculated. Various experiments were carried out with different additives.

Weight Loss Experiment: The method for the preparation of mild steel test coupons, cleaning them and measuring the surface area were same as that described in a previous communication[2]. Corrosion rate was expressed in mg/sq. dm/day. The coupons were kept immersed by means of glass hooks in water samples with various additives in wide mouth polythene bottles. The containers were kept in a thermostat maintained at 40°±0.1°C. Air was bubbled through the containers by means of a suction pump.

Experiments to study the effect of pH on the rate of reversion were carried out in pure water and also after adding to water suitable amounts of (a) NH_4NO_3 (500 ppm)+NaCl (40 ppm), and adjusting the pH of the solutions to the required values (Fig. 1, Table 1).

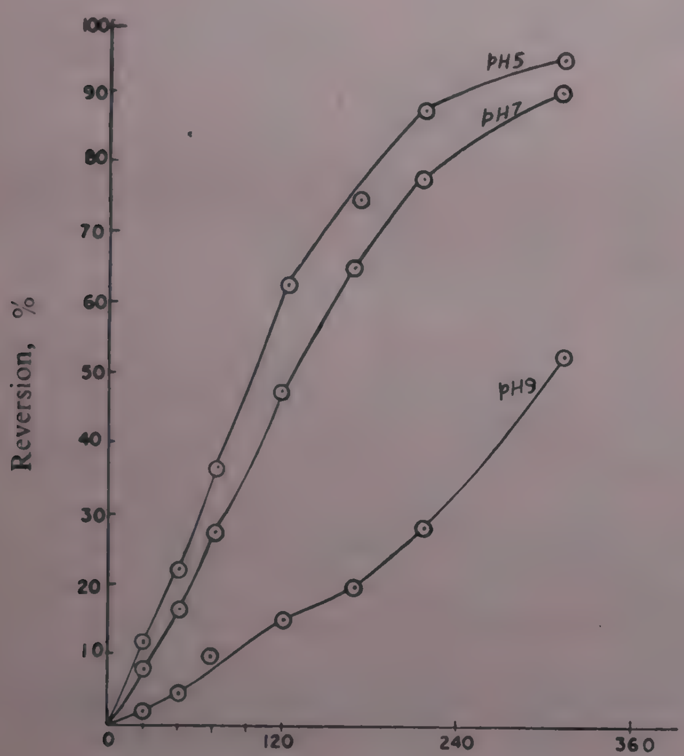


Fig. 1—Effect of pH on the Reversion of Sodium Polyphosphate in pure water at 40°C.

Various additives were added to water samples and the effect on the rate of reversion was observed (Table 2).

The effect of addition of different amounts of potassium sulphate and aluminium sulphate in water, at a temperature of 40°C was also studied. The results are given in Table 3.

The effect of addition of various amounts of santobrite, magnesium sulphate and aluminium sulphate on the rate of reversion of polyphosphate in cooling tower water at a pH of 7.0 and temperature 40°C are given in Table 4 and Fig. 2.

TABLE 2—Reversion of Sodium Polyphosphate (Synthetic) in Prepared Water Samples in Presence of Various Substances

(pH—7.0; Mw=13.000; Temp. 40°C)
Conc. of polyphosphate 18.6 ppm

Material Used	*Concentration, ppm.*	*Reversion After 48 hr, %*
BLANK	—	17.78
Hexamine	100	28.93
	200	27.92
Carboxy Methyl Cellulose ..	300	21.33
Urea	300	10.67
Dextrine	300	14.72
Glucose	20	9.63
Starch	300	8.63
Gum Acacia	20	15.23
	100	19.80
Glycerol	20	13.71
	300	11.67
Santobrite	10	16.13
	30	7.53
	50	2.88
Magnesium Sulphate ..	100	7.10
	200	2.28
	300	2.28
Potash Alum	100	8.60
	200	1.34
	300	1.34

TABLE 3—Effect of Santobrite on the Reversion of Commercial Sodium Polyphosphate in Synthetic Water

(Concentration of Polyphosphate 18.6 ppm; pH 7.0; Temp. 40°C)

	Reversion, %		
Time, hr	*10, ppm*	*30, ppm*	*50, ppm*
24	8.6	4.30	1.07
48	16.13	7.53	2.88
96	43.55	13.93	11.29
120	62.49	30.10	24.73
144	78.52	46.24	35.48
168	91.94	65.05	40.86
192	100.0	78.50	62.37

TABLE 4—Effect of Potassium Sulphate and Aluminium Sulphate on the Reversion of Sodium Polyphosphate in Synthetic Water and Process Water

(pH 7.0; Temp. 40°C)

Time, hr	% Reversion, Chromate (20 ppm) and Polyphosphate (18.8 ppm) in Synthetic Water (pot. sulphate)			% Reversion, Chromate (20 ppm) and Polyphosphate (18.8 ppm) in Synthetic Water (aluminium sulphate)			% Reversion, Chromate (20 ppm), Polyphosphate (18.8 ppm) in Process Water (aluminium sulphate)		
	18 ppm	*37 ppm*	*55 ppm*	*36 ppm*	*72 ppm*	*108 ppm*	*36 ppm*	*72 ppm*	*108 ppm*
24	15.07	15.07	15.07	4.16	4.16	4.16	8.24	6.92	6.92
48	28.25	25.53	25.53	6.92	6.92	6.92	8.24	8.24	8.24
72	36.17	36.17	32.44	8.24	6.92	6.92	8.24	8.24	8.24
120	46.82	44.16	44.16	8.24	6.92	6.92	12.23	8.24	8.24
168	68.08	68.08	68.08	8.24	6.92	6.92	12.23	12.23	12.23

TABLE 5—Effect of Potash Alum on the Reversion of Polyphosphate in Pure and Process Water Under Different Conditions

(Temp. 40°C; pH 7.0)

Time, hr	% Reversion, Chromate (20 ppm), Polyphosphate (18.6 ppm) in Pure Distilled Water					% Reversion, Polyphosphate (18.8 ppm) in Process Water				% Reversion, Polyphosphate (18.8 ppm) Chromate (20 ppm) in Process Water		
	Blank	*50 ppm*	*100 ppm*	*200 ppm*	*300 ppm*	*Blank*	*100 ppm*	*200 ppm*	*300 ppm*	*100 ppm*	*200 ppm*	*300 ppm*
24	11.29	3.22	0.00	0.00	0.00	16.38	4.26	0.53	0.53	4.57	0.53	0.53
48	23.39	11.29	8.60	0.54	0.54	30.77	9.57	9.57	9.57	9.57	9.57	9.57
72	35.48	16.63	8.60	1.34	1.34	36.14	10.90	10.90	10.90	10.57	9.57	9.57
96	—	—	—	—	—	41.49	—	—	—	—	—	—
120	46.67	19.32	11.29	3.22	3.22	—	17.55	12.23	12.23	13.55	12.23	12.23
168	62.37	23.66	11.29	8.60	8.60	—	—	—	—	—	—	—
192	—	—	—	—	—	52.21	20.21	13.55	13.55	17.55	13.55	13.55

TABLE 6—Effect of Potash Alum on the Reversion of Sodium Polyphosphate in Synthetic Water

(pH 7; Temp. 40°C; Initial Concentration of Polyphosphate 18.7 as PO_4)

Time, hr	% Reversion, Chromate (20 ppm) without Aeration					% Reversion, Chromate without Aeration			% Reversion, Chromate (40 ppm) with Aeration During Corrosion Testing		
	Blank	*50 ppm*	*100 ppm*	*200 ppm*	*300 ppm*	*Blank*	*100 ppm*	*200 ppm*	*Blank*	*100 ppm*	*200 ppm*
24	13.10	11.77	0.53	0.53	0.53	9.57	1.59	1.59	8.47	1.59	1.59
48	35.87	14.44	8.55	5.08	3.74	20.23	2.92	1.59	20.21	1.59	1.59
72	46.57	15.14	8.55	6.42	3.74	30.85	4.26	2.92	26.86	2.92	2.92
96	51.93	27.81	8.55	6.42	3.74	40.80	4.26	2.92	36.00	2.92	2.92
120	—	—	—	—	—	52.12	9.47	2.92	44.16	4.26	2.92
144	62.62	30.49	8.55	6.42	3.74	—	—	—	—	—	—
168	—	—	—	—	—	68.08	10.90	2.92	57.44	6.92	2.92
192	84.04	35.83	8.55	8.55	6.42	—	—	—	—	—	—

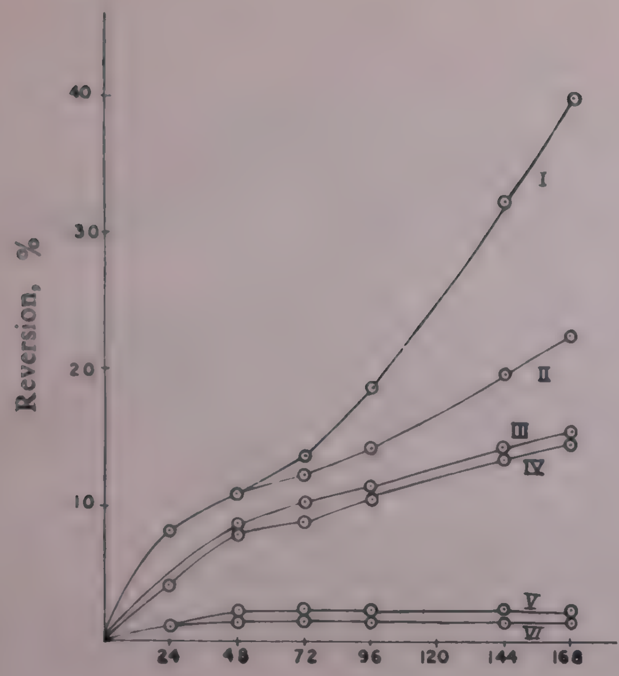


Fig. 2—Effect of Various Additives on the Reversion of Sodium Polyphosphate in Natural Water of Ammonia Plant Cooling Tower.

I—Blank
II—Santobrite (50 ppm)
III—Magnesium Sulphate (100 ppm)
IV—Magnesium Sulphate (100 ppm)+Santobrite (50 ppm)
V—Aluminium Sulphate (36 ppm)
VI—Aluminium Sulphate (108 ppm)

The effect of 50, 100 and 200 ppm potash alum was studied on the reversion of polyphosphate with aeration, without aeration and in the presence of the corrosion test coupon at pH 7 and 40°C (Table 5). Similar studies were also carried out with process water in presence of chromate (Table 6).

Corrosion testing of mild steel in water samples, containing polyphosphate (20 ppm) and chromate (40 ppm), was also carried out under conditions of continuous aeration. The pH and temperature of the solutions were maintained at 7.0 and 40°C respectively. Experiments were also performed in presence of dissolved alum. The corrosion rates in mg/sq. dm/day are given in Table 7.

Discussion

It will be observed from Fig. 1 that the rate of reversion of polyphosphate in pure water decreases as the pH increases. Similar effect of pH was also observed by previous workers[19,26]. Under the same conditions of temperature and pH, the reversion rate is higher in prepared water sample and also in the presence of ammonium nitrate (500 ppm) and mixtures of ammo-

TABLE 7—EFFECT OF CHROMATE POLYPHOSPHATE AND POTASH ALUM ON THE CORROSION RATE OF MILD STEEL

(pH 7; Temp. 40°C)

Duration 24 hr

Combination of Inhibitors Used	*Aeration, period/day*	*Corrosion Rate, mg./sq. dm./day*	*Remarks*
(i) Synthetic water alone	11 hr.	185.6	Sludge formed
(ii) Synthetic water + chromate (40 ppm) + polyphosphate (20)	,,	11.15	Very Slight Sludge
(iii) Synthetic water + chromate (40 ppm) + polyphosphate (20 ppm) + pot. Alum (300 ppm)	,,	46.18	Slight Sludge
(iv) Synthetic water	15 hr.	190.0	Sludge Formed
(v) Synthetic water + chromate (40 ppm) + polyphosphate (20 ppm)	,,	2.6	Very Slight Sludge Formed
(vi) Synthetic water + chromate (40 ppm) + polyphosphate (20 ppm) + pot. Alum (200 ppm)	,,	4.94	Slight Sludge
(vii) Synthetic water + chromate (40 ppm) + polyphosphate (20 ppm) + Pot. Alum (100 ppm)	,,	4.60	Very Slight Sludge
			Duration 5 days
(a) Synthetic water + chromate (40 ppm) + polyphosphate (20 ppm)	Continuous Aeration	0.65	Very Slight Sludge
(b) Synthetic water + chromate (40 ppm) + polyphosphate (20 ppm) + pot. Alum (100 ppm)	,,	2.35	,,
(c) Synthetic water + chromate (40 ppm) + polyphosphate (20 ppm) + Pol. Alum (200 ppm)	,,	4.37	,,

nium nitrate (500 ppm) and sodium chloride (40 ppm) than in pure water (Fig. 1 and Table 1). Since ammonium nitrate increases the rate of reversion of polyphosphate its consumption would tend to be heavy in ammonia plant cooling tower water which usually contains an appreciable quantity of ammonium nitrate[2].

From Table 2 it is clear that some additives definitely have a retarding effect on the rate of reversion of sodium polyphosphate in water. Agents which diminish the rate of reversion are d-glucose, starch, gum acacia, glycerol, santobrite, magnesium sulphate and potash alum. Among them only magnesium sulphate, santobrite and potash alum have significant effect under the conditions existing in the cooling tower (Fig. 2 and Tables 3 and 4).

From the comparative study of the effect of potassium sulphate and aluminium sulphate (Table 4) on the rate of reversion of sodium polyphosphate in process water and in the sample prepared in the laboratory it is clear that the Al^{3+} ion is responsible for controlling the rate of reversion while potassium sulphate is ineffective. The effectiveness was found to increase with an increasing amount of potash alum (Tables 5 and 6) both in presence and absence of chromate and also in corrosion and inhibition studies.

Since polyphosphate is frequently added in conjunction with chromate in cooling waters to inhibit corrosion of mild steel, weight-loss experiments were carried out in water samples treated with chromate+polyphosphate with or without a further addition of alum. The results (Table 7) show that inhibition is not affected by the presence of alum and sludge formation is very little. The addition of some Al^{3+} in cooling waters may therefore be considered as a means to decrease the rate of reversion of polyphosphate. The most suitable concentration for controlling reversion would seem to be 100-200 ppm of potash alum which corresponds to 7.4 to 14.8 ppm of Al^{3+}.

The behaviour of Mg^{2+} ion to retard the rate of reversion has been explained on the basis of formation of stable chelates and these chelates have a low degree of hydrolysis[19]. The behaviour of Al^{3+} ion in retarding the rate of reversion can also be explained on the same basis.

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Degradation Products of Humic Substances with Alkaline Potassium Permanganate and their Identification by Paper Chromatography

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A comparative investigation on the degradation products with alkaline potassium permanganate of humic acids obtained from soil as well as from coal was made. Both the samples yielded a large number of amino acids and polyphenols, which were identified by means of ascending, descending and circular paper chromatographic techniques using a number of solvents and location reagents. The compounds identified were α-amino n-valeric acid; α-alanine; tyrosine; cystamine; serine; lysine; histidine and other amino acids along with iso-homovanillic acid; 2,4 dihydroxy acetophenone; 2,5 dihydroxy benzaldehyde; 2,3 dihydroxy benzoic acid from soil, whereas those from coal yielded α-amino n-valeric acid; α-alanine; tyrosine; anthranilic acid; p-amino benzoic acid; s-benzyl pencillamine; β-phenyl ethylamine and imidazole carboxylic acid along with some other phenolic compounds like 3,4 dihydroxyphenyl acetic acid; 3,4 dihydroxyacetophenone; phloroglucinol; phloro-glucinol carboxylic acid; 4, hydroxy aceto phenone and 4-hydroxy benzaldehyde. Based on the above facts it has been assumed that both soil and coal humic acids molecules are of heteropolycondensate type which are formed during the process of humification.

In an earlier communication[1], the extraction of humic acids sample from soil using mild sodium hydroxide and its purification from carbohydrates and other sugars using ion exchange column has been described. In all, eight components—as ascertained by paper chromatography—in both the organic solvent soluble and insoluble fractions of humic acids have been reported, while the same solvents yielded three components in fulvic acids. Attempts have since been made for the identification of these components, and the present communication describes studies carried out on the degradation products of humic substances with a view to identify the products of oxidation by paper chromatography.

The use of potassium permanganate as an oxidant for the degradation of humic acids and related compounds has been suggested[2], but the substances identified did not provide much elucidation of the structural relationship of humic acids. However, the report of Schnitzer and Desjardius[3] is of importance in analysing the degradation products of humic acids by gas chromatography. The authors have chosen here the same oxidant and used various standard solvents, colouring reagents and Rf values in determining the chemical nature of the compounds obtained as degradation products. A similar effort has been made recently by Steck and Wender[4] in estimating free phenolic hydroxyl groups of a large number of phenolic compounds by the descending technique, while the analysis of the various fractions of the degradation products of humic acids have been carried out mostly by the ascending technique. The use of circular and descending techniques have been made wherever such comparable results could be available. At least three solvents and a number of colouring reagents have been used to identify the chemical nature of the compounds.

Experimental

The humic acids used in this work were procured from two different sources: (i) A soil sample having pH 8.25 was taken from this Division's experimental farm. The extraction and purification of humic acid was carried out by the process already described[1]. The sample has been designated as HA-1. (ii) A lignite

sample was provided by a Swiss firm, Messrs Chemische Fabrick, under the trade name 'Fluka'. It was used as such. This sample has been referred as HA-2.

The oxidation of both the samples was carried out in Pyrex glass conical flasks at 55°±0.5°C in constant temperature bath. The potassium permanganate solution was added in small quantities and the oxidation was carried out for 15 hours. The precipitated manganese dioxide was removed by centrifugation. The addition of potassium permanganate was stopped when a faint permanganate colour persisted overnight. The excess permanganate was decomposed by adding a few drops of redistilled ethanol. Table 1 indicates the respective amount of humic substances used, potassium permanganate required and change in colour during oxidation of the two samples.

The fractionation of the degradation products was carried out with 10% W/V solution of barium chloride (A.R.) and the schematic procedure used in both the cases is described below.

TABLE 1—AMOUNT OF HUMIC ACID AND POTASSIUM PERMANGANATE USED

Nature of Sample	*Wt. of Humic Acid Oxidized g.*	*Wt. of Solid $KMnO_4$ Reqd., g.*	*Humic Acid $KMnO_4$*	*Colour of Humic acid in NaOH Soln.*	*Colour of Oxidized Products*
Extracted from Soil (HA-1)	5.0	7.5	1:1.5	Brown	Yellow
From Lignite (HA-2)	10.0	25.0	1:.2.5	Dark-Brown	Brownish Yellow

Results and Discussion

The fractions S_1, S_2 and S_3 contained the major part of the degradation products of soil and coal humic acids. The Rf. values obtained by ascending, descending and circular paper chromatography have been compared with those of Smith[5], Steck and Wender[4] and Chartier[6] et al. (Tables 2-4).

SCHEME No. 1 for HA—1

Degradation product + 10% W/V $BaCl_2$

Yellow Precipitate: Dissolved the precipitate in 1.0 N-HCl and filtered

Filtrate: (colourless-rejected).

Filtrate: A 10% solution of H_2SO_4 was added until no further precipitation was observed. The contents were kept overnight and filtered.

No residue.

Filtrate: Light yellow, evaporated on water-bath to dryness and re-extracted with water.

Precipitate: $BaSO_4$ (rejected)

Filtrate: Light Brown colour; desalted electrolytically and chromatographed. (S_1)

Solid residue (not analysed)

SCHEME No. 2 for HA—2

Degradation Product + 10% W/V $BaCl_2$

Precipitate: Washed with distilled water; dissolved in 1.0 N—HCl and filtered.

Filtrate: Light yellow colour; evaporated on water-bath and re-extracted with distilled water. The colour changed from light yellow to deep orange. The solution was electrolytically desalted and chromatographed (S_3)

Filtrate: Deep yellow colour with brownish tinge; 10% solution of H_2SO_4 was added to remove Barium ions and filtered

Residue (in traces) rejected.

Filtrate: Evaporated on water-bath to dryness and extracted with water. Desalted electrolytically and chromatographed. (S_2)

Residue: (rejected)

The results on oxidative degradation of humic acids and the subsequent colour changes represented the degree of browning phenomenon as suggested by Scheffer and Ulrich[7] in humification of soil and coal humic substances (Table 1). The humic acid : permanganate ratio suggests that high molecular amorphous heteropolycondensates of coal humic acids form much more complex molecules than those from soil humic acids. In fact these higher molecular heteropolycondensates seem to be responsible for different types of colour changes during oxidation, fractionation, evaporation and drying.

An examination of Tables 2 and 4 suggests that the degraded amino acid molecules play a vital role in soil microbial reaction. Table 4 indicates that Rf values and the nature of bands with ninhydrin in

TABLE 2—Rf. VALUES (× 100) AND COLOUR REACTIONS IN STANDARD SOLVENTS RECOMMENDED BY SMITH* FOR ASCENDING CHROMATOGRAPHY

	SOLVENTS								*LOCATION REAGENTS*					
Fractions	*n. Butanol + Acetic acid + Water (12:3:5) (V/V)*		*n. Butanol + Pyridine + Water (1:1:1) (V/V)*		*Methanol + Pyridine + Water (16:0.8:4) (V/V)*		*Ethanol + Water + Ammonia (18:1:1) (V/V)*		*Nihydrin*	*Sulphanilic acid (diaz.)*	*Nitroso-naphthol*	*B.C.G.*	*D.Q.C.*	*Compounds Identified*
	Observed	*Standard**	*Observed*	*Standard**	*Observed*	*Standard**	*Observed*	*Standard**						
	54.7	56	—	—	64.8	66	48.2	47	Purple	—	—	Yellow	—	Amino n. valeric acid.
	30.8	30	38	37	54	52	32	33	Purple	—	—	Yellow	—	Alanine.
S_1	43.0	45	62	60	53	50	—	—	Purple	—	Pink red	—	—	Tyrosine.
	36.5	37	67	66	65.5	64	54	55	Purple	—	—	Blue	—	Cysteamine.
	24.5	22	31	33	42.5	42	21.5	20	Purple	—	—	—	—	Serine
	13.8	12	15	13	13.4	15	—	—	Brown	Light Orange	—	—	Bluish grey.	Lysine
	55.6	56	—	—	65	66	46.8	47	Purple	—	—	—	—	Amino n-valeric acid
	96.0	95	—	—	75	77	40.2	41	—	—	—	Yellow	—	Anthranalic acid.
	88.7	88	74.5	75	73	74	27.5	26	—	—	—	,,	—	Amino benzoic acid.
S_2	82.8	82	70	71	64	62	—	—	Purple	—	—	—	—	S-Benzyl pencillamine.
	76.8	76	78	80	75.6	77	—	—	,,	—	—	Blue	—	Phenyl ethylamine.
	29.1	30	36	37	55	52	31	33	,,	—	—	—	—	Alanine.
	46.0	45	61	60	54	50	—	—	,,	—	Pink red	—	—	Tyrosine.
S_3	28.2	26	36	32	—	—	—	—	Purple	Brown	—	Yellow	—	Imidazole carboxylic acid.

NOTE: *The standard values have been taken from Tables 5.3, 5.4, 5.5 and 5.6, pages 89-94 of *Chromatographic and Electrophoretic Technique* Vol. I, Ivor Smith, (Interscience Publishers Inc., New York), 1960.
B.C.G.—Bromo-cresol green.
D.Q.C.—2:6 Dichloroquinone chloroimide.

TABLE 3—RF VALUES (× 100) AND COLOUR REACTIONS IN BENZENE + ACETIC ACID + WATER (125 : 72 : 3 V/V) BY DESCENDING TECHNIQUE

Fraction	Sulphanilic acid (diaz.)		p-Nitroaniline (diaz.)		Ferric Chloride		$FeCl_3$+ $K_3Fe(CN)_6$		B.C.G.		D.Q.C.		Standard* Values	Compounds Identified
	Colour	Rf.	Colour	Rf.	Colour	Rf.	Colour	Rf.	Colour	Rf.	Colour	Rf.		
	Orange (fade)	75.0	Rose pink	75.0	Yellow (Faint)	64	Bluish (green)	73.0	Yellow	86.0	Blue	77.0	75.0 or 76.0	Iso-homo vanillic acid or Iso vanillic acid or 2, 4 dihydroxy acetophenone.
S_1	Yellow (deep)	62.0	Rose pink	63.0	—	—	Sky blue	61.0	Blue	73.0	—	—	62.0 or 63.0	Hydroxy Coumarin or 2, 5 dihydroxy benzaldehyde.
	Yellow	42.0	Rose pink	49.0	—	—	-do-	49.0	Yellow	32.0	—	—	43.0	2, 3 Dihydroxy Benzoic acid.
	Yellow	36.0	Rose pink	35.1	—	—	—	—	faint Yellow	56.6	—	—	36.0 or 37.0	3, 4 Dihydroxy phenyl acetic acid or 3, 4 Dihydroxy acetophenone.
S_2	Yellow	6.8	,,	5.4	—	—	—	—	Yellow	35.4	—	—	8.0 or 6.0	Fluoro glucinol or Fluoro glucinol carboxylic acid.
	Orange (fade)	72.0	Rose pink	62.1	Deep brown	73.7	Yellow pink	61.2	Deep blue	66.7	Grey	76.4	73.0	3 Hydroxy benzaldehyde.
S_3	—	—	,,	50.6	faint Brown.	50.8	Bluish purple.	43.3	Yellow	48.2	Red	67.0	66.0 or 67.0	4, Hydroxy benzoic acid.

standard solvent 1 are almost exactly the same but some discrepancies in Rf values are noted when the results are computed in standard solvents 2 and 3. This may be due to the method of preparation of the two solvents. Solvent 2 was prepared by heating tert. butanol and solvent 3 by taking 2 : 6 lutidine in place of 2 : 4 lutidine which was not available. The Rf values which could not be computed have been bracketed. The presence of histidine-type compound, which could not be detected by the ascending technique, suggests the presence of imidazole type structure in the degradation products of both soil and coal humic substances.

Table 2 provides additional information about the heteropolycondensates, as the compound identified in fraction S_2 mostly contains an aromatic nucleus. The existence of conjugated double bond nucleus becomes more prominent when the identified products of Table 3 are taken into account. The presence of S-benzylpencillamine is of particular interest because no direct test for the presence of sulphur in humic acids molecule could be detected, but on the basis of Rf values and colour reactions its presence has been found. The presence of tyrosine, α-amino n-valeric acid and α-alanine are also of interest as these are present in the degradation products of both types of molecules viz. HA-1 and HA-2. Table 3 provides information for the type of phenolic compounds present in various fractions. The colour reactions with p-nitroaniline and ferric chloride-ferric cyanide reagents provide additional confirmation for these compounds. Although rose pink colour is a characteristic colour for sinapic and ferulic acids type compounds, these are not supported by their Rf values[4]. A characteristic colour of pink-violet type is observed with ferric chloride-ferric cyanide reaction but the Rf values and other colour

TABLE 4—COMPARISON OF RF. VALUES BY CIRCULAR PAPER CHROMATOGRAPHY (RF. VALUES × 100)

Sl. No.	Group Amino Acids	*n. Butanol + M. E. Ketone + Water + Ammonia (5:3:1:1 V/V)*				*Tert. Butanol + Formic Acid + Water (75:0.8:24.2 V/V)*				*2:6 Lutidine + Water (2:1 V/V)*			
		*Standard**	S_1	S_2	S_3	*Standard**	S_1	S_2	S_3	*Standard**	S_1	S_2	S_3
1.	Cysteine	7		—	—	26	96	(95)	(70.6)	—	(84)	—	—
	Glutamic acid	—	—	—	—	39	86	(88)	(57.3)	—	(59)	—	—
	Aspartic acid	—	—	—	—	48	84	—	(45.3)	—	—	—	—
2.	Lysine	12.15	12.5;15.0	14	—	—	—	—	—	17	17	13	18
	Arginine	—	—	—	—	—	—	—	—	25	23	25	25
	Glycine												
	Hydroxyproline	—	—	—	—	—	—	—	—	39	32	28	—
		—	—	—	—	—	—	—	—	—	37	35	—
3.	Histidine	20	22	21	21	76	78	79	—	—	—	—	—
	Alanine	—	—	—	—	50	—	50	—	—	—	—	—
	Serine	—	—	—	—	38	—	—	—	—	—	—	—
4.	Tyrosine	28	28.5	26.5	25	—	—	—	—	65	67	—	61
	Valine	—	—	—	—	—	—	—	—	44	—	43	—
	Methionine	—	—	—	—	—	—	—	—	51	49	—	—
	Proline	—	—	—	—	—	—	—	—	—	—	—	—
5.	Threonine	33	—	34	30	37	—	—	36.6	—	—	—	—
6.	Isoleucine	41	41.2	41.5	—	63	62	60.6	—	—	—	—	—
	Leucine phenylalanine	46	—	47.7	45	53	—	—	52.0	—	—	—	—

Note:—* The standard values have been taken from *J. Chromatography*, **1** (1958) 317.

1. The Rf. values bracketed have not been accounted on the basis of the above table which indicates the existence of some different compounds than what have been taken in this table.
2. In place of 2:4 Lutidine, 2:6 Lutidine has been taken.

reactions again do not correspond for the presence of pholoroacetophenone and salicylic acid.

Acknowledgement

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Ureolytic Bacteria in Soil II—Their Prevalence and Activity in Different Soils of Bihar

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The presence of ureolytic bacteria in a great majority (69-100 per cent) of soil samples, collected from twenty centres representing different agro-climatic regions of Bihar, has been demonstrated. The rate of urea hydrolysis obtained by these organisms in liquid medium is slow during the first 24 hours but is fairly rapid during the second and third day with more or less complete transformation in 5-7 days. The importance of these results with respect to soil application of urea for crop production has been discussed.

The question of urea hydrolysis and its rate in soil must be carefully considered for proper utilization of this source of nitrogen for crop production. Urea is hydrolyzed by an enzyme, *urease*, which can be elaborated in soils by many soil micro-organisms including bacteria, fungi and algae and a number of higher green plants. Though a knowledge of the relative importance of each of these groups of organisms in cultivated soils with respect to urea transformation is much desired, little is known at present. A study on the problem has, therefore, been taken up.

Amongst all the micro-organisms present in soil, bacteria probably are much more numerous than any other single group. The biochemical activities of these microbes, therefore, may play important roles in soil plant relationships. In an earlier communication[1], the presence of ureolytic bacteria in the soils of the newly developed farm of this division and a method of their detection have been discussed. The results on the prevalence of this biochemical group of organisms and the intensity of their activity in different soils of Bihar are presented here. Similar observations on soil fungi and algae will be reported in due course.

Methods and Materials

The technique for the detection of ureolytic bacteria in soils has already been described in details[1]. According to this, sterilized liquid medium containing urea is inoculated by a little amount of soil or a few pieces of thoroughly washed organic matter isolated from soils to be tested. If ureolytic microbes are present, they grow out of the inoculum and catalyse the hydrolysis of urea into ammonia and carbon dioxide. As a result, the reaction of the liquid medium changes towards alkalinity which is easily detected with the help of phenol red indicator incorporated therein.

In order to assess as many soil samples as possible, small test tubes (100×12 mm.) containing 2-3 ml. of the liquid medium with phenol red were sterilized and carried to the field in sufficient number. These had been packed in suitable containers to avoid contamination during transit. The tubes were unpacked only after reaching the sites and were immediately inoculated by fresh soils collected aseptically from layers about 1″ below the soil surface with the help of a spatula, the sterilization of which was done by flaming immediately before and after each soil collection. All attempts were made to keep the quantity of soil inoculum as uniform as possible at least in volume by using the flattened but bent end of a spatula. Random samples were taken from cultivators' field, at least 50 tubes being inoculated from each village thus comprising 50 samples. Two such villages, generally neighbouring ones, had been sampled at each centre. Immediately after inoculation, the mouths of the tubes were carefully flamed, well plugged and the tubes were then

packed again in containers. All samples had been collected during June, 1965. In order to get the representative data for all soil types and climatic zones of the state, 20 centres had been selected throughout Bihar, the locations of which are shown in map (Fig. 1).

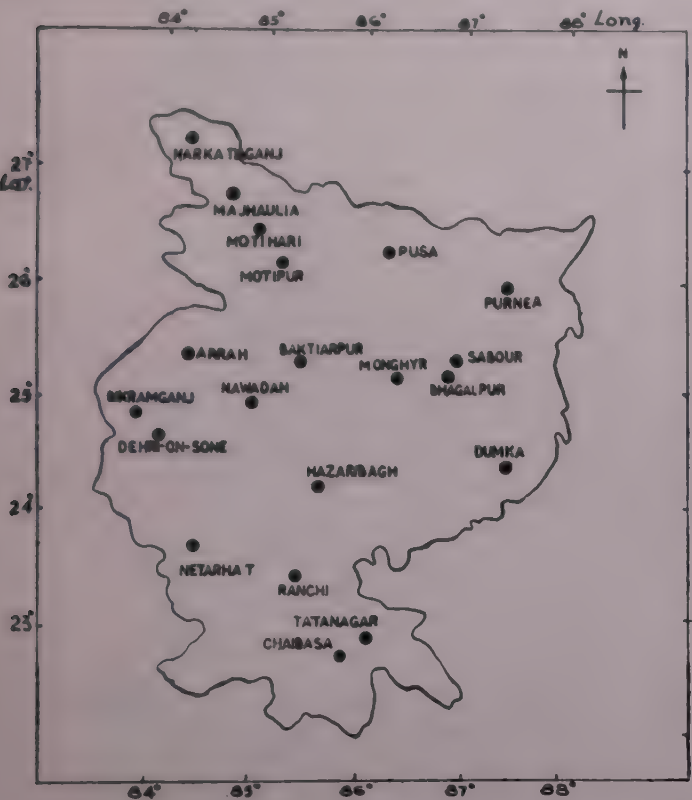

Fig. 1—Map of Bihar Showing Places of Soil Collection.

After returning to the laboratory urea (fertilizer grade), sterilized by drying at 80°C for 2 hours, was added to all the tubes which were then incubated at room temperature (28-34°) for 5 days. At the end of this period, the number of tubes showing the evidence of urea hydrolysis (as is judged by the change of colour of media from yellow to red due to change in pH) was noted and expressed as percentage. This field survey was supplemented by another series of experiments conducted in the laboratory. Duplicate soil samples in sufficient quantity had been collected simultaneously for this purpose. In these cases, all samples collected from each centre were kept in one sterilized container giving a composite sample for each centre. After thoroughly mixing, a portion of this was taken out and pieces of partly decomposed organic matter were isolated. These were then thoroughly washed in sterilized water by several changes and used as inoculum. After incubating for 5 days at room temperature, the percentage of tubes showing change of colour of media was noted as in the previous case with soil inoculum.

For quantitative estimation of the intensity of urea hydrolysis by mixed culture of micro-organism, 100 ml. of the same media (without indicator) taken in 250 ml. flasks was sterilized and inoculated by (1) about 0.2-0.3 g. of a well mixed soil sample in the first series and by (2) 2-3 pieces of washed organic matter in the second. After adding urea to a concentration of 500-600 ppm. nitrogen, the flasks were incubated at room temperature for several days and the quantity of ammoniacal nitrogen released as a result of urea hydrolysis was estimated at regular intervals by Nessler's reagent colorimetrically. Controls were always maintained to check all possible sources of error.

The pH of soil samples was determined by a Cambridge pH meter using a glass-calomel electrode. For this purpose air-dry soil was taken in water in 1 : 2.5 ratio and allowed to be soaked for 2-3 hours with occasional shaking. Organic carbon was estimated by Walkley and Black's method.

Experimental Results

The results on the prevalence of ureolytic bacteria in soils of Bihar are presented in Table 2. Some brief characteristics of soils used are shown in Table 1.

It is evident from the data (Table 2) that in the series of experiments using soil as inoculum, the greater majority of samples (69 to 100 per cent) of all centres so far tested harbour bacterial population capable of hydrolysing urea. While cent per cent of all soil samples from Hazaribagh, Ranchi, Netarhat, Pusa, Dehri-on-sone, Bikramganj, Bakhtiarpur, Sabour, Dumka and Bhagalpur yielded positive indication of their presence, the corresponding figures for Chaibasa, Jamshedpur, Motipur, Motihari, Narkatigunj, Majhaulia, Arrah, Nawada, Purnea and Monghyr are 81, 85, 93, 92, 90, 90, 96, 69, 95 and 95 respectively. Thus, only a small percentage of samples (4 to 31 per cent) from 10 centres did not yield any ureolytic bacteria. Under field conditions, this is quite understandable as some local adverse conditions are likely to influence the microbial population in some isolated pockets here and there but in view of their wide prevalence, this is likely to be temporary in nature.

The relationship of these organisms with soil organic matter under field conditions warrants close examination. For this purpose, pieces of organic matter isolated from soils and then thoroughly washed in serial changes of sterile water to wash out the loosely adhering organisms had been used as inoculum. It is evident from the results shown in column 2 of Table 2 that a great majority (80-100 per cent) of the organic matter even though they are thoroughly washed by shaking, are

TABLE 1—BRIEF CHARACTERISTICS OF SOILS USED

Location of Centres	Villages of Soil Collection	Soil Types	Organic Carbon, %	pH
1. Hazaribagh	Lakhe & Korha	Yellow loam	0.76	6.0
2. Ranchi	Nagri & Gorakhshini	-do-	0.42	6.0
3. Netarhat	Jamtoli & Bartoli	Red loam	1.20	5.4
4. Chaibasa	Gitirpi-1 & Gitirpi-2	Mixed red and black	0.45	6.0
5. Jamshedpur	Paddi-1 & Paddi-2	-do-	0.68	5.9
6. Motipur	Mahual and Berji	Alluvium calcareous	0.55	8.5
7. Motihari	Lakshmipur and Sanker Saryia	-do-	0.84	9.1
8. Narkatiaganj	Laligarhi and Maldahya	Alluvium non-calcareous	0.55	6.1
9. Pusa farm	Bhugrasan and Paddy Block	Alluvium calcareous	0.47	9.2
10. Majhaulia	Mohiddipur and Chailagarh	-do-	0.59	8.5
11. Dehri-on-Sone	Berkop and Chainpur	Alluvium heavy soil	0.51	8.2
12. Bikramganj	Sajni and Ghusia	-do-	0.72	6.3
13. Arrah	Akona and Aneity	-do-	0.63	6.5
14. Bakhtiarpur	Madhupur 1 and 2	-do-	0.63	8.3
15. Nawada	Mangalbigha 1 and 2	-do-	0.59	7.2
16. Purnea	Banbhaga and Praura	Alluvium	0.59	6.0
17. Sabour farm	Maize and Paddy plots	-do-	0.80	8.1
18. Dumka	Asansol and Murabahal	Red and Yellow loam	0.63	6.5
19. Bhagalpur	Khiraban and Baijani	Alluvium heavy soil	0.80	7.2
20. Monghyr	Bhojichak and Ramnagar	-do-	0.59	8.0

TABLE 2—SOIL SAMPLES SHOWING THE PRESENCE OF UREOLYTIC BACTERIA, %

Location	Nature of Inoculum Used	
	Soil	Washed Organic Matter
Hazaribagh	100	100
Ranchi	100	100
Netarhat	100	100
Chaibasa	81	80
Jamshedpur	85	100
Motipur	93	96
Motihari	92	80
Narkatiaganj	90	84
Pusa	100	100
Majhaulia	90	80
Dehri-on-Sone	100	95
Bikramganj	100	85
Arrah	96	80
Bakhtiarpur	100	90
Nawada	69	100
Purnea	95	100
Sabour	100	90
Dumka	100	100
Bhagalpur	100	100
Monghyr	95	80

capable of yielding ureolytic bacteria in liquid media. It only shows that this biochemical group of microbes probably belonging to different non-related toxonomical forms is intimately associated with organic components of soils and perhaps taking active parts in colonising them. Such organisms are deep-seated in the tissues of organic matter and hence are not removable by mechanical shaking. Thus, the facts that ureolytic bacteria are abundant in soils and are intimately associated with its organic components, clearly indicate that they are well established in soils though some local conditions may affect the population rather adversely in some isolated pockets.

The results on the intensity of urea hydrolysis by mixed culture of soil micro-organisms are presented in Fig. 2. Both soil and washed organic matter had been used as inoculum separately for this purpose but the results obtained in both the series were more or less identical. It may be noted from the graphs (Fig. 2) that the rate of urea hydrolysis as judged by the concentration of ammonia is slow during the first 24 hours but it increases quite sharply thereafter. This trend is more or less the same with soils from all centres so far examined, though the detectable amount of ammonia present in solution after 4 days varied considerably in different cases. Thus, with soil inoculum from 19 out of 20 centres (vide Table 3) more than 50 per cent of urea has been hydrolysed in 4 days and the nitrogen thus transformed can be accounted for as ammonia in solution.

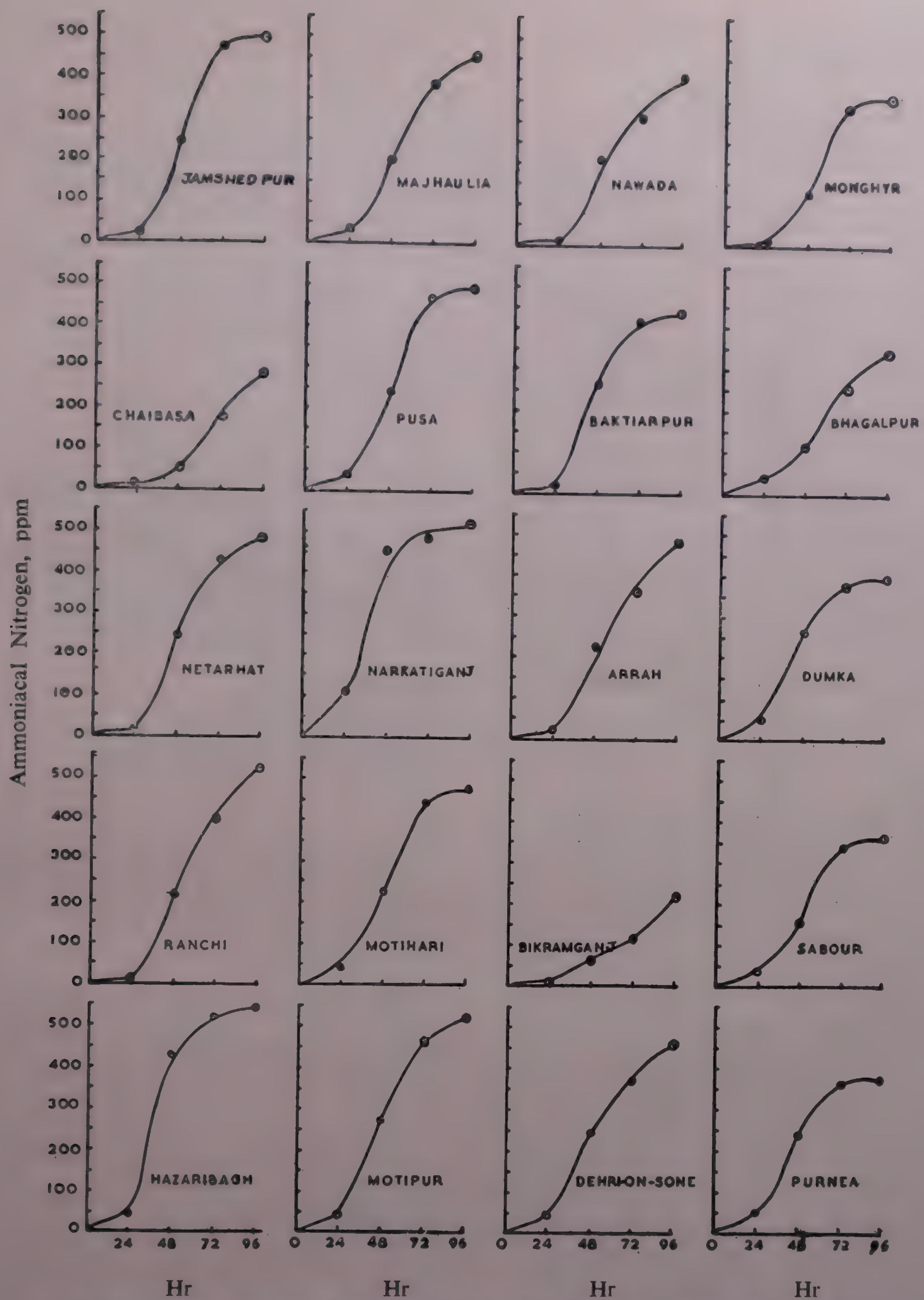

Fig. 2—Intensity of Urea Hydrolysis by Mixed Culture of Soil Micro-organisms.

The total disappearance of urea, however, was noted in almost all cases in 5 to 7 days. The estimation of ammoniacal nitrogen in solution at the end of this period (5-7 days), however, always yielded lower figures than those obtained earlier (up to 3-4 days). This is mostly due to the loss of ammonia through volatilization and partly to its utilization by organisms.

It may be noted from the graphs (Fig. 2) that in most of the cases, the rate of urea hydrolysis is maximum during the second and third days of incubation but tends to decline thereafter. This is probably due to the decrease of urea concentration and the development of high alkalinity in solution with time as a result of its hydrolysis.

Conclusion

The prevalence of ureolytic micro-organisms in the soils of Bihar and the rapidity of their activity in liquid

TABLE 3—Hydrolysis of Urea in Liquid Media Inoculated by Soil

(After 4 days' incubation)

Location	*Ammoniacal Nitrogen, ppm.*	*Hydrolysis, %*
1. Hazaribagh	540	98.2
2. Ranchi	525	95.5
3. Netarhat	480	87.3
4. Chaibasa	285	51.8
5. Jamshedpur	480	87.3
6. Motipur	520	86.0
7. Motihari	470	81.0
8. Narkatiganj	520	86.6
9. Pusa	495	85.3
10. Majhaulia	455	78.4
11. Dehri-on-Sone	460	83.6
12. Bikramganj	220	40.0
13. Arrah	480	87.3
14. Bakhtiarpur	440	80.0
15. Nawada	410	74.5
16. Purnea	370	75.0
17. Sabour	360	72.0
18. Dumka	400	80.0
19. Bhagalpur	347	69.4
20. Monghyr	360	72.0

cultures have been discussed. Though these microbes may be adversely affected in some isolated pockets, the evidences indicate that they are widely distributed in almost all the soils of this State and are intimately associated with its organic components. It seems, therefore, that they are well established in these soils and perhaps also possess the ability to decompose organic matter in addition to their ureolytic property. The soil application of urea as fertilizers is, therefore, likely to be followed by its hydrolysis within a few days. As a result, ammonia may accumulate to an appreciable toxic concentration. If applied superficially on soil surface, which is the general practice at present, a substantial amount of nitrogen may be lost through volatilization. Thus, although urea is a concentrated fertilizer with lower cost of production, its proper utilization can only be ensured by adopting suitable measures aimed at minimizing the hazards of toxicity and volatilization loss. The research on these problems has already been taken up and will be reported soon.

Acknowledgement

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Design Principles Governing Pole Line Construction

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The article provides a special reference to economical pole line construction. A comparative study is made for three different types of line supports where the design of brace channel pole has been picked up to be the cheapest. To provide co-ordination between the foundation and the super-structure, an analysis is presented to arrange the resisting moment to be greater than the over-turning moment and thus provide a safety factor against over-turning. Besides intermediate structures, the poles to be used at angle and dead end locations have also been dealt with to make the designer as well as the field engineer familiar with the technical implications involved both in design and construction. The use of concreted stay sets has also been described and recommended in preference to the naked stay sets as the concreted stay sets are not only safe against corrosion, but also obtain additional strength. The co-ordination to be maintained between the stay plate, stay rod, and the stay wire has also been stressed to ensure their safe design. The erection of plinth foundations at various situations has also been described with particular reference to their economical construction.

Before extra-high voltages of 66 KV and above were developed and introduced for our transmission systems all lines were normally carried on poles or small lattice structures. As the load demands increased rapidly at centres far distant from the sources of the power generation, long transmission lines had to be designed on towers with large span construction. Tower construction is a special feature which will be discussed separately. For the present pole line construction falls within the purview of this note.

The author is prompted to write this paper to familiarize the reader with the mechanical design of transmission lines erected on poles. Several lines were observed to have fallen because of employment of faulty design conventions and practices. In certain instances rail poles were erected without muffs and no coordination existed between the foundation and the super-structure. The foundations were weak and could not produce enough resisting moment to counteract the overturning moment due to super-imposed loading of windage, etc. The foundations gave way and the entire line collapsed. Similar incidents occurred on a line erected with built-up structures not provided with muffs or concrete foundations. It will, therefore, be appreciated that the foundations should be designed to have adequate strength. Besides foundation failures, collapsing of structures was also not uncommon when pipe poles with inadequate strength were used. Disposal pipes were used for transmission lines in large number and also beams were employed when drawn poles and rails were in short supply.

Beams and rails are very weak in the longitudinal direction as compared to their strength in the transverse direction. The Electricity Rule which provides that the strength of the structures in the longitudinal direction should in no case be less than one-fourth the strength required in the transverse direction, prohibits their economical use. Beams, rails and pipe poles, therefore, cannot be economically employed for line construction. Built-up structures have, therefore, been brought into use which the author had designed for the Punjab State Electricity Board in the form of lattice structure, braced channel poles, stepped channel poles, etc., which are now being used widely for transmission lines up to 33 KV and also for distribution and service lines in rural and urban areas. The economy of a construction does not merely lie in the fact that it is cheaply erected. It would be false economy if the construction is not efficient and safe. The designer has, therefore, to keep in view economy combined with efficiency, and he will have to be familiar with the correct design

principles and conventions which the author has tried to incorporate hereunder.

Line Supports

The line support could be a steel tubular pole, rail, beam, wooden pole, concrete pole or a fabricated lattice structure or a built-up structure with channels or beams or stepped channel or beam structure. Normally intermediate structures are designed to carry a dead load of conductor or conductors and earth wire, insulators, cross-arms plus the weight of one man with tools, hand lines, etc. and the windage on conductor, earth wire and structure itself. The windage or wind loading is calculated on the basis of the wind span and the wind pressure of the region which the line is to traverse. The intermediate structure is not usually designed for any line deviation or broken wire conditions. Any support not conforming to these conditions and loading will not be suitable for use as an intermediate structure unless provided with wind stays which will be an uneconomical proposition. This reminds the writer of a 33 KV line erected on 90 lb. rails with bundled conductors of 7/0.136″ copper. Collapsing of these structures and their foundations was frequently occurring on this line during stormy weather till wind stays at every fourth or fifth pole were provided. It was obviously a case of faulty design and erection. When a line support is designed it has got to be ensured that it gives the required margin of safety. For instance, under the Indian Electricity Rules the following factors of safety are specified:

The Minimum Factors of Safety for Line Support based on Crippling Load

(*i*)	Metal supports	2.2†
(*ii*)	For mechanically processed concrete supports	2.5
(*iii*)	For hand-moulded concrete supports ..	3.0
(*iv*)	For wood supports	3.5

In this context a comparative study of three types of line supports is presented. The line under study is a single circuit 33 KV line with 7/0.161″ S.C.A. conductors. The normal span to be kept is 400 ft. and the line is to traverse through a 15 lb. per sq. foot wind pressure region.

Wind load per span on one conductor $=\frac{2}{3}\times 15\times\frac{0.483}{12}\times 400=161$ lbs., where 0.483″ is the diam. of the conductor.

†This figure is 2.0 according to the latest IEE Rules. Ed.

The formation of conductors is shown in Fig. 1. Equivalent wind load of three conductors at 1 ft. below top $=\frac{1}{27}(161\times\frac{117^*}{4}+2\times 161\times\frac{101^*}{4})$ (Fig. 1)

$=476$ lb.

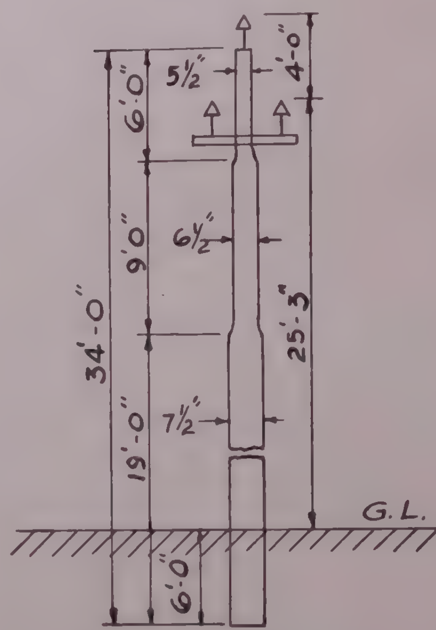

Fig. 1.

Steel Tubular Pole

Taking a pole $7\frac{1}{2}''\times 19'$, $6\frac{1}{2}''\times 9'$, $5\frac{1}{2}''\times 6'$,
Weight of pole $=668$ lb.

Safe working load based on crippling load $=\frac{1516}{2.2}$ lb.

$=690$ lb.

Windage on pole by sections:
Section 1—$15\times 2/3\times 15/24\times 13=81.2$ lb.
Section 2—$15\times 2/3\times 13/24\times 9=48.7$ lb.
Section 3—$15\times 2/3\times 11/24\times 6=27.5$ lb.
Equivalent wind load corresponding to windage on pole at 1 ft. below top $=\frac{1}{27}[(81.2\times 6.5)+(48.7\times 17.5)+(27.5\times 25)]=77$ lb.

$\therefore$ the total working load on pole $=(476+77)$ lb. $=553$ lb.

The pole which can carry 690 lb. safe working load is, therefore, more than safe.

Rail Pole 90 lb.

Equivalent wind load corresponding to windage on

$^*\frac{117}{4}$ and $\frac{101}{4}$ are the equivalents of 29′-3″ and 25′-3″.

rail pole at 1 ft. below top $=\frac{15\times5.375^{**}}{12}\times28\times\frac{28}{2}\times\frac{1}{27}$ lb.

$=97.5$ lb.

$\therefore$ Total working load on pole $=(476+97.5)$ lb.
$=573.5$ lb.

$\therefore$ Overturning moment $=573.5\times27$ ft. lb.

Section modulus required $=\frac{573.5\times27\times12}{8\dagger\times2240}$
$=10.37$ inch^3

The section modulus for 90 lb. rail is 13.05 inch^3. The rail pole is, therefore, safe.

But in this case it is to be ensured that the section modulus of the rail in the longitudinal direction is not less than 2.59 inch^3.

Braced Channel Pole

For the same working load of 600 lb. the weight of the braced channel pole comes to 450 lb. The design of the braced channel pole will be discussed separately. It may be seen that for the same loading the weight of the steel tubular pole is 668 lb.; rail pole 1020 lb., and of braced channel pole only 450 lb. It will, therefore, be economical to design the braced channel poles for this type of line construction keeping in view the strength stipulated to be obtained in the longitudinal direction.

Single Support Foundation

The properties of soil being not so definite as those of other materials, the design of a single support foundation becomes a little complex. However, for design calculations it is normally assumed that there is no elasticity in the soil and it has a maximum rupturing stress proportionate to the depth. The point of fulcrum is taken as $\frac{H}{\sqrt{2}}$ below ground level and the formula used for the resisting moment is $\frac{KDH^3}{10}$ lb.inch, where K is assumed to vary between 2000 to 4000; D is the average diameter of pole in ground-inch; H=depth of pole below ground level-feet.

To illustrate the use of this formula let us take the case of a steel tubular pole, earlier designed as a support for a 33 KV line and find out the diameter of the muff which would be required to give additional surface area in contact with the soil to make the foundation safe against over-turning.

Depth of pole buried in ground $=6$ ft.

Depth of point of fulcrum $=\frac{6}{\sqrt{2}}$ ft.
$=4.2$ ft.

Wind load due to windage on conductors and pole acting 1 ft. below top $=553$ lb.

Height of point of load above fulcrum point $=(27+4.2)$ ft.
$=31.2$ ft.

$\therefore$ Max. overturning moment due to windage $=553\times31.2$ lb. ft.

Resisting moment of ground assuming K equal to 2000 $=\frac{2000\times D\times6^3}{10\times12}$

The resisting moment shall be more than the overturning moment.

$$\therefore \frac{2000\times D\times6^3}{10\times12}=\geqslant553\times31.2$$

$$\therefore D\geqslant\frac{553\times31.2\times10\times12}{2000\times6\times6\times6}$$

$$=\frac{553\times31.2\times5}{18000}=\frac{553\times31.2}{3600}$$

$=4.8$ inches.

The diameter of the pole in ground is $7\frac{1}{2}$. There is, therefore, no need to use the muff so far as the strength of the foundation is concerned, but there are other considerations which require shielding of steel when buried in ground. The steel is liable to be corroded when in contact with the soil. In some highly corrosive areas the naked steel poles and stay sets when buried in ground are eaten up so quickly that one can hardly imagine such a phenomenon to occur. The muffs or concrete foundations approximately $1\frac{1}{4}''$ thick are normally provided around depths of steel structures in ground to give adequate protection against corrosion. Therefore, concrete foundations for steel structures are provided for strength as well as to avoid corrosion. The structure shall have a safety factor against overturning or in other words the resisting moment shall be greater than the overturning moment. The foundation designed as such will be amply safe against dead loads as shown hereunder :

The safe bearing pressure of earth=2240 lb./sq. ft.

Bearing area of pole $=\frac{\pi}{4}\times\left(\frac{10}{22}\right)^2$ sq. ft., here the dia-

**5. 375 is the base width in inches of the 90 lb rail on which the windage is assumed to be acting.

†8 represents the safe tensile stress for steel in tons per sq. inch.

meter of pole with muff in ground is 10 inch.

Total dead load of pole, conductors, cross arms and one man with tools, etc. $=1200^{*}$ lb.

$$\therefore 2240\times\frac{\pi}{4}\times\frac{100}{144} 7 1200$$

or 1222 7 1200

Therefore the foundation is safe against thrust.

Stays and Stay Sets: The stays could be divided into 3 categories : (a) wind stays, (b) stays used at angle locations, (c) stays used at dead ends.

As mentioned earlier the wind stays are only employed when the structures are not of adequate strength to withstand the super-imposed loading. The minimum factor of safety as specified under the Indian Electricity Rules is 2.5 for the stay wires, stay rods and stay plates, which means the tension in the stay wire is not to exceed 40% of its ultimate strength. Now supposing the total working load on the structure is 690 lbs. and its safe working load is only 550 lbs. the balance (690—550 lb.) i.e. 140 lb. load shall be taken care of by the stay set, which shall be designed accordingly. The wind stays are provided on both sides of the structure normal to the line as the windage could occur from either direction.

Fig. 2 shows a wind stay which is put up to take care of the wind load W. If the stay wire makes an angle θ with the ground and T is the tension in the stay wire,

$W=T\cos\theta$

$$\therefore T=\frac{W}{\cos\theta}=W\sec\theta$$

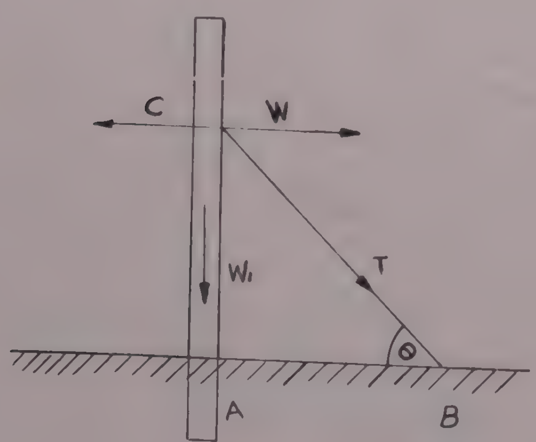

Fig. 2.

* This figure is made up roughly of
290 lb—weight of 3 conductors
180 lb—weight of one man with tools
668 lb—weight of pole
62 lb—weight of cross arms and insulators
1200 lb

This tension T will have also a component W_1 which will act as a dead load and adds to the thrust.

$W_1=T\sin\theta$

$$=\frac{W}{\cos\theta}\sin\theta=W\tan\theta$$

It may be observed that to keep T low we have to make AB as large as could be possible.

The stays are also used at angle locations where the line deviates. Fig. 3 shows a line deviating at an angle

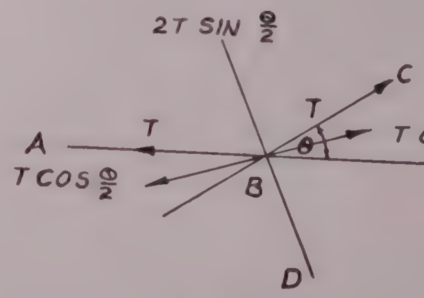

Fig. 3.

of $\theta°$. The stay will be put up in the direction BD which bisects the angle ABC. If T be tension of the conductor, then the tension in the stay wire$=2T\sin\frac{\theta}{2}$.

According to I.E. rules the tension in stay wire is not to exceed 40 per cent of its ultimate strength. It is, therefore, necessary to select a stay wire of the size which would allow that much margin of safety once the working tension is known.

Similarly at dead end location the stay or the multiple stays have to counterbalance the full tension of the conductor or conductors and the stay wires are to be designed accordingly.

Stay Rod

Stay rod is always installed in line with the stay wire and it shall, therefore, be capable of developing the maximum strength of the stay wire. Allowing a factor of safety 2.5 the safe tensile strength of steel is 8 tons per sq. inch.

If a be the sectional area of the stay rod in square inch working load of the stay rod$=(8\times2240\times a)$ lb.

$\geqslant=$working tension of the stay wire

$\geqslant=T$ lb.

$$\therefore a\geqslant=\frac{T}{8\times2240}$$

Stay Plate

The stay plate will engage the frustum of inverted

pyramid of earth with an angle of repose of 30° with the vertical. This angle of repose is different for different soils. For less adhesive soils such as sandy and marshy soils where the angle of repose is very small concrete is used to obtain the required strength of the stay set. For normal clay soils as are generally encountered, angle of repose can safely be taken as 30°. The friction of the body of earth in which this pyramid is framed provides ample factor of safety. But for calculation purposes and to maintain design coordination, stay plate shall be designed to have a strength slightly greater than the stay rod.

In Fig. 4 abcd is the stay or the anchor plate and h is the depth of plate below ground level. Corresponding to the side ab of the plate the side of the pyramid at ground level is ($ab+2\ \theta\ \tan\theta$), where θ is the angle of repose with the vertical. Similarly for the side bc

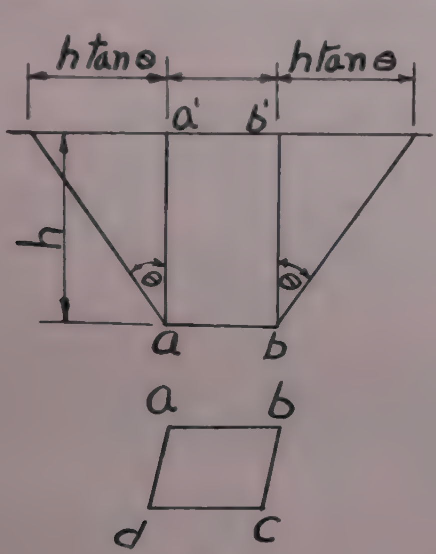

Fig. 4.

it is ($bc+2h\tan\theta$)

Area of the plate $= ab \times bc$

$=$ say A sq. inch

Area at the ground level

$= (b+2h\tan\theta)\ (c+2h\tan\theta)$

$=$ say B sq. inch

$\therefore$ volume of the pyramid

$$= \frac{h}{3}(A+B+\sqrt{AB})$$

The earth weighs 90 lb. per cubic ft.

or 0.0522 lb. per cubic inch

$\therefore$ weight of inverted pyramid of earth

$$= \frac{h}{3} \times (A+B+\sqrt{AB})\ 0.0522\ \text{lb.}$$

This weight of earth shall be greater than the load in lb. which the stay rod shall carry. The stay plate could, therefore, be designed to fulfil this condition. There have been instances when naked stay sets buried in ground were uprooted as the stay plates or the stay rods were eaten up by rust and ultimately yielded. This resulted in the collapsing of structures or even long stretches of transmission and distribution lines. The concreted stay sets have, therefore, been brought into use which have proved to be a success and have already started giving dividend. The collapsing of structures or lines due to failure of stay sets is now rare. The stay sets where concreted are not only safe against corrosion but also have additional strength.

The stay plate is in shear whereas the stay rod is in tension. The safe shear stress of steel is roughly 10,000 to 12,000 lb./sq. inch. The area of stay plate under shear stress is that which comes under the nut or the nut and the washer, if any provided, fixed at the end of the stay rod. The greater this area the larger will be the shear strength of the plate. To make this area greater, the plates are sometimes cast in the shape shown in Fig. 5. The cast iron plates are normally designed with that shape as the cast iron has a low shear stress. These plates are sometimes reinforced to get additional strength when required.

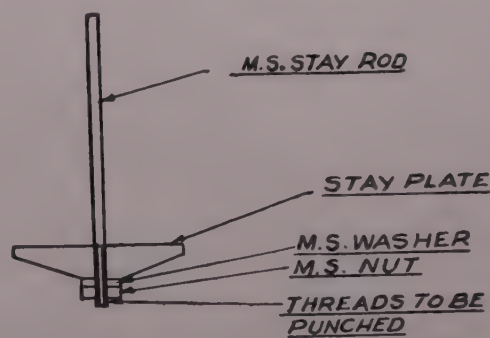

Fig. 5.

Plinth Foundations

The structures are provided with plinth foundations when the lines cross marshy, sandy or wet soils. Raised plinth foundations are also erected to obtain proper ground clearances at road and railway crossings or when poles with suitable lengths are not available. It once happened that on a certain 33 KV line feeding an important load centre, 3 pipe poles of weak section collapsed at the ground level. The whole place was muddy, slushy and marshy all round due to heavy rains which made the transport of the new poles to site utterly impossible. The same poles had, therefore, to be cut at the ground level and used with reinforced raised plinth foundations.

Because of less depth of pole buried in ground the plinth had to provide the balance resisting moment.

Pole diam. with muff in ground=9 inches.
Original pole depth in ground=6 ft.
∴Original resisting moment provided by the ground

$$=\frac{2000\times9\times6^3}{10\times12}\text{ lb. ft.}$$

∴ Resisting moment with 2 ft. pole in ground

$$=\frac{2000\times9\times2^3}{10\times12}\text{ lb. ft.}$$

$$\therefore\text{ Balance resisting moment }=\frac{2000\times9}{10\times12}(6^3\text{-}2^3)\text{ lb. ft.}$$

$$=\frac{2000\times9}{10\times12}\times208=\frac{124800}{4}=31200\text{ lb. ft.}$$

The plinth foundation shall be so designed as to give:

(1) proper bonding with the pole,

(2) requisite bearing area to resist thrust due to dead loads,

(3) requisite surface area in contact with the soil below ground level.

Let the plinth be a square foundation with the side equal to a ft., depth below ground level equal to 3 ft. and height above ground level equal to $1\frac{1}{2}$ ft.

$$\text{Resisting moment*}=\frac{2000\times27\times a}{6}=31200$$

$$\therefore a=\frac{31200\times6}{2000\times27}$$

$$=3.5\text{ ft.}$$

The designer has the privilege to effect compromise between the results obtained through empirical formulae and those based on his practical experience.

This square foundation with 3.5 ft. side will be amply safe against thrust as the bearing pressure $3.5\times3.5\times2240$ lb. is much greater than the dead load which the pole has to carry.

Conclusions

Transmission and distribution lines should be properly designed before erection. It is never wise to make haphazard use of structures as this would result in uneconomical construction.

Coordination shall be maintained between the strengths of structures and their foundations i.e. the foundation shall be designed to be stronger than the structure.

Similar coordination should be maintained between the strengths of the stay wire, stay rod and stay plate. Whenever stays are put up, stay plate shall be designed to be stronger than the stay rod and the stay rod to be stronger than the stay wire.

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*In the formula for resisting moment, the figure 10 has been substituted by 6 as the flat surface is in contact with the soil instead of round surface.

Coke Oven Gas as a Feedstock for Ammonia Production*

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The food situation facing the country has pushed into prominence the many-sided and complex issues of overcoming the agricultural lag. For achieving self-reliance in food production, there is no escape from chemicalization of agriculture, for which the conditions whereby indigenous processes and products based upon indigenous know-how and raw materials are best utilized are essential.

Coke oven gas, one of the cheapest sources of hydrogen particularly when it is available as surplus or where its use in furnaces and steelworks, can be replaced by a cheaper fuel, can provide a premium feestock for ammonia. Thus the rapidly growing iron and steel industry of the country can simultaneously assist in stepping up nitrogenous fertilizer production from indigenous sources by releasing its valuable by-product, viz. coke oven gas; where blast furnace gas is plentiful, it can also be utilized with coke oven gas for conversion to ammonia and then to urea—thus, steel and nitrogenous fertilizer industries can be profitably integrated. In fact, if all the coke oven gas associated with steel production were to be harnessed for manufacture of nitrogenous fertilizer, additional nitrogen production from this source alone would be 0.8 m. te. per annum, which is a substantial portion of the projected additions and capable of being processed from a purely indigenous raw material.

By low temperature fractionation of the purified coke oven gas, a synthesis mixture of hydrogen and nitrogen can be produced while the hydrocarbon fractions are separated out and could be returned for use as fuel. In a variation, coke oven gas can be steam-reformed catalytically, and blast furnace gas (where available) can provide the heating medium for the reformation furnace as well as to supplement carbon dioxide. In a further variation, blast furnace gas can be added into the product gases from steam catalytic reformation of coke oven gas and a nitrogen/hydrogen mixture brought to tolerances using methanation for finishing operation in purification.

Coke oven gas contains hydrogen and hydrocarbon-rich volatile fraction evolved during carbonization of coal in closed, indirectly-heated retorts or ovens. Readily condensable or easily recoverable valuable by-products, viz. ammonia, benzene, toluene, etc., from this fraction are usually removed as a first step in the by-product recovery sections of the carbonization units themselves. Quite often this purification step extends to removal of inorganic sulphur compounds too, especially where the gas is used as a fuel. Residual gas after these operations can serve as a very desirable feedstock for ammonia synthesis. The paper mainly concerns itself with discussing possible processing techniques for production of ammonia from the above carbonization by-products.

In choosing a processing technique, many basic considerations may intervene. A prime one would be the availability of the gas. Coke oven gas is normally used as a fuel where it is available as a by-product. Merchant ovens use from 40 to 50 per cent of the total gas produced for meeting heat requirements for underfiring the ovens. Where a commercial outlet for the excess coke oven gas exists, it is sold as a fuel at fairly high prices in keeping with its higher calorific value and luminous flame characteristics. In steelworks, the excess is blended with other fuels (like blast furnace gas) and utilized for miscellaneous heating applications, mainly where a higher calorific value or a luminous flame is desired. Since coke oven gas is rich in hydrogen and can also be completely processed to an ammonia synthesis mixture using comparatively attractive and economic processes, it should be utilized for manufacture of ammonia wherever there is a reasonable chance to get it released for that purpose.

*Paper presented at the Seminar on Hydrogen Production and Utilization in Petroleum Refining and Petrochemical Industries held under the auspices of the Indian Institute of Petroleum, Dehra Dun, U. P. during March 19-21, 1966.

Where surplus coke oven gas is available, the availability can most conveniently be expressed as a total heat value rather than in volumetric terms. A typical composition of high temperature carbonization gas would show that while hydrogen predominates volumetrically, it effectively contributes only 34 per cent of the heating value of the gas (Table 1). The primary

TABLE 1—COMPOSITIONS OF FEED GASES, % BY VOL.

Components	*Coke Oven Gas*	*Blast Furnace Gas*
Carbon Dioxide	3.0	15.9
Carbon Monoxide	8.5	25.6
Hydrogen	57.00	3.3
Methane	26.0	—
Ethylene	2.8	—
Nitrogen	2.2	54.4
Argon	—	0.6
Oxygen	0.5	0.2
Sulphur	1200 ppm	500 ppm
Total	100.00	100.00

purpose of any feedstock for ammonia is to furnish hydrogen, the nitrogen being generally recovered from air, either by physical methods like low temperature fractionation or chemically by combination of oxygen and extraction of resultant compounds. It would appear therefore, that where availability in terms of heat value is limited, extraction of hydrogen from the coke oven gas, with return of the rich fractions back to fuel mains, could furnish a most effective method of using the gas, provided the economics of processing suit this method. The availability of coke oven gas, however, cannot be determined merely on the basis of whether the gas produced is completely utilized in the process or not. The assessment should also extend to a study of how far substitute fuels (preferably by-products which have little other use in the process or sources which cannot easily or economically yield synthesis gas directly) can be used to replace the coke oven gas at its traditional usage points and release corresponding feedstock for ammonia production. The investment for provision of substitute fuels should naturally be treated as a charge on the fertilizer plant while reciprocity should be maintained by charging outgoing and incoming fuel to the parent project on a par for costing purposes. Arising from the above, it is also apparent that where both feedstock as well as fuel for fertilizer production are to be considered, all available surplus potential fuel in the parent project must be covered and a fully integrated picture built up in order to project a most comprehensive and economic usage pattern. Such surplus fuels include nut coke from coke ovens which can be gasified to give lean gas, other categories of lean fuel such as blast furnace gas from iron works; non-coking coal for production of richer producer gas etc.

Process Routes to Ammonia from Coke Oven Gas

The main process routes for coke oven gas to ammonia synthesis gas are illustrated in flowsheets (Figs 1-3).

Low Temperature Fractionation: The first one (Fig. 1) follows the classic pattern adopted in Rourkela where gas substantially freed from readily condensable aromatics, hydrogen sulphide, etc. (in Rourkela this is done under pressure) is compressed to synthesis pressures—usually in the vicinity of 13 atm—freed from carbon dioxide, usually by ammonia and caustic wash,

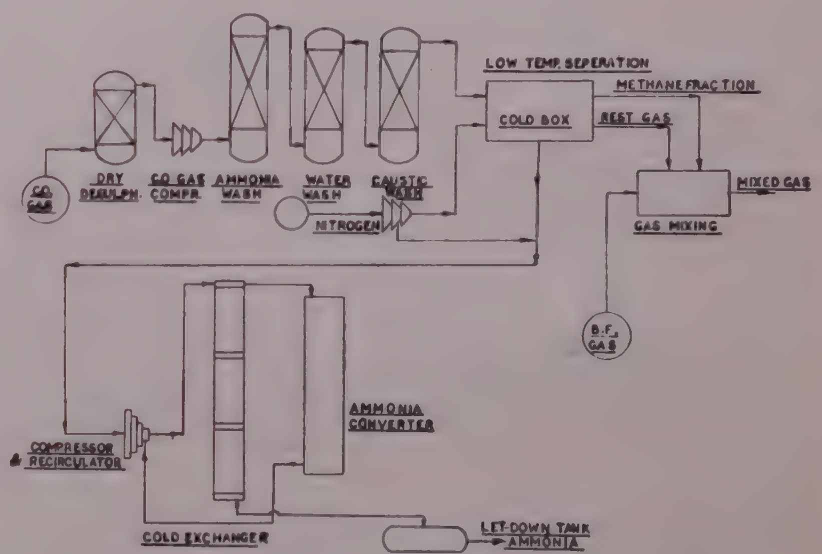

Fig. 1—Low Temperature Fractionation of Coke Oven Gas.

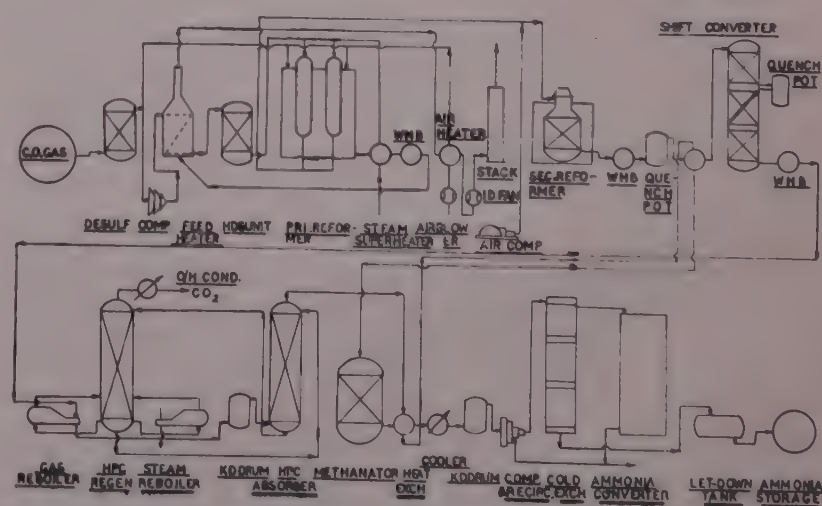

Fig. 2—Steam Reformation of Coke Oven Gas.

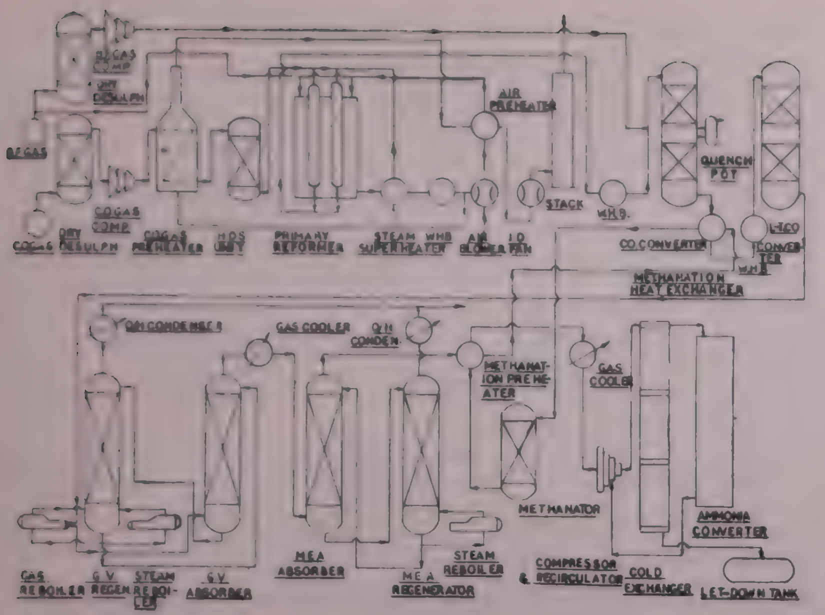

Fig. 3—Reformation of Coke Oven Gas Utilizing Blast Furnace Gas.

and then in successive stages reduced in temperature to condense out the hydrocarbons. While the first stages of cooling, viz. down to —40°C, is done by ammonia refrigeration, cooling down to around —110°C is accomplished by heat exchange with outgoing vaporized hydrocarbon fractions now let down to nearer atmospheric pressures. Further reduction of temperatures down to —191°C is effected by a high pressure nitrogen gas recycle and all hydrocarbons down to methane are condensed out. The gas is finally given a wash with liquid nitrogen which removes last traces of carbon monoxide leaving a nitrogen-hydrogen mixture which is adjusted to synthesis gas proportion by supplementary nitrogen. After recovery of "cold" from this gas, it is released at ambient temperature for further processing to ammonia. The various hydrocarbon fractions collected in the above procedure can be either sent back as an enriched fuel fraction or suitably blended with lean gas to adjust calorific values to original intake gas levels.

The above procedure has been advantageously utilized in Rourkela. Nitrogen necessary for supplementing the hydrogen was readily available from the oxygen plant, which is an ancillary unit for the L-D process. For conversion of ammonia to a solid fertilizer however, this process restricts a choice on end products to ammonium nitrate, or ammonium sulphate/chloride. The latter can be manufactured only where sulphuric or hydrochloric acid are available. The gypsum process is not applicable for sulphate production in the absence of a sufficiently extensive output of carbon dioxide as a by-product in ammonia production operations. The ammonium nitrate as such being not considered safe for marketing as fertilizer, has to be blended with limestone to furnish a product with 20.5 per cent nitrogen.

Steam Reformation: An alternative approach could be tried out where synthesis grade nitrogen is not readily available for use or sufficient carbon dioxide for conversion of ammonia to urea has also to be recovered. The scheme is illustrated in Fig. 2. The procedure follows more or less the technique and sequence of operations used in the most recent plants for processing natural gas. Compressed coke oven gas is put through a hydro-desulphurization-cum-zinc oxide contacting step—which incidentally reduces the unsaturates content to acceptably low limits—to remove organic sulphur and put through a steam catalytic reformer. Blast furnace gas, enriched to extent necessary by coke oven gas, can be used as the fuel for the reforming furnaces. This is followed by a secondary reformer where the requisite nitrogen is added; then follows CO-conversion in two or more stages to reduce CO to 0.3 per cent, followed by carbon dioxide removal down to 0.3 per cent, and methanation before release of prepared synthesis mixture for ammonia production. Carbon dioxide obtained as a by-product in this process will, however, be insufficient to convert all the ammonia to urea. If this has to be supplemented a collateral unit may be set up in which, dust-free, clean, blast furnace gas is compressed, put through a CO-conversion step, stripped of carbon dioxide in a potash wash scrubber, and an enriched fuel fraction containing mainly nitrogen, hydrogen and unconverted carbon monoxide is released back to fuel mains. A good process economy can be secured if heat released in CO-conversion could be used for regeneration of the carbon dioxide from circulating potash, and on pressure release, power could be recovered to drive the initial compressor. The gas, stripped of carbon dioxide, could very well contribute to the fuel requirements of the reformer furnace.

Reformation Utilizing Blast Furnace Gas: An improvement on the above procedure is represented in Fig. 3. In this case, the primary reformation is carried out to a more advanced stage than in the case just discussed above, the hydrocarbon residuals being reduced to less than 1 per cent. The process gas stream from this reformer is supplemented by a stream of cleaned and desulphurized blast furnace gas which would contribute both nitrogen and carbon dioxide to the system. The combined stream could now be put through CO-conversion, carbon dioxide removal, and methanation prior to release to synthesis. This scheme represents an

improvement over the previous one (Fig. 2), since the blast furnace gas not only furnishes carbon dioxide, but also contributes some hydrogen as well as nitrogen. Moreover, the hydrogen-rich stream of primary reformed gas obtained in the previous method would normally lose about 8 per cent of potential hydrogen in the reactions with oxygen (from secondary air) in the secondary reformer. This loss is avoided. But the more rigorous limits to which primary reforming of coke oven gas is to be carried out would call for a higher endothermic heat input in the primary reformer furnace and correspondingly put up the fuel requirements.

Investment Costs

Indicative requirements in terms of investment for process and service plants for each of the above alternatives have been presented in Table 2, while Table 3 correspondingly summarizes the operating costs. The supplementary tables explain unit costs and characteristics of materials and utilities on which the derivations in Table 2 have been based. The following broad observations may be made: The scheme for extraction of hydrogen alone from coke oven gas would come out in its best light where the parent project can spare only coke oven gas. The procedure would ensure maximum extraction of ready-made hydrogen, with minimum reduction in fuel calories, and with little degradation in calorific values of the return fuel. The process is mainly power intensive and not fuel intensive. The equipment required are fairly sophisticated and are normally only available as completely fabricated package units from abroad. Foreign exchange as well as investment costs may be fairly higher than for the other two alternatives. The scheme would permit of conversion of ammonia to only one of its salts, and not to urea unless a source of carbon dioxide is located and tapped.

The second scheme, excluding CO_2 recovery from blast furnace or lean gas, would work out attractive where both a source of lean fuel (like the blast furnace or producer gas) as well as coke oven gas are available for disposal. For the main feed stream it should be the endeavour to secure as much of the coke oven gas as possible by substituting lean fuel gas wherever practicable (for firing coke ovens, reformer furnace, etc.) The carbon dioxide recovery from the main stream may be insufficient for conversion of all the ammonia to urea unless a supplementary source is tapped to augment the output. Many of the equipment involved are such as could be easily fabricated within the country. Even the more sophisticated section like reformation could be engineered within the country under licenses from

TABLE 2—INVESTMENT COST

Basic Capacity: 600 te/day Ammonia *All figures in Rs. lakhs*

Sl. No.	*Items*	*Alternative I*		*Alternative II*		*Alternative III*	
		Total	*F.C.*	*Total*	*F.C.*	*Total*	*F.C.*
1.	Equipment supply FOB/FOR, inclusive of design, engineering, procurement and process royalties	698.89	508.73	581.18	378.58	549.79	381.30
2.	Additional charges like freight, transport and handling, customs, sales tax etc. before equipment is delivered to site ..	240.51	—	179.03	—	176.75	—
3.	Expenditure at site to install the plant	166.45	26.00	134.40	18.50	127.36	17.61
4.	Other facilities like plant lighting, cooling towers, etc ..	33.20	4.00	32.20	3.84	34.10	4.10
	Total ..	1139.05	538.73	926.81	400.92	888.00	403.10

Note: Alternative I—Low temperature fractionation to recover exclusively hydrogen from coke oven gas.

Alternative II—Steam-reforming of coke oven gas without supplementary carbon dioxide recovery facilities.

Alternative III—Steam-reforming of coke oven gas with addition of blast furnace gas to reformed gas stream to supply nitrogen and carbon dioxide sufficient for ultimate conversion of ammonia to urea.

TABLE 3—PRODUCTION COSTS

Costs—Rs./te Ammonia *Basic Capacity—6000 te/day ammonia*

Sl. No.	*Items*	*Alternative I*	*Alternative II*	*Alternative III*
1.	Raw Materials	72.53	85.90	88.36
2.	Utilities	85.54	50.86	60.32
3.	Other charges	47.03	37.81	35.78
	Works cost:—	205.10	174.57	184.46
4.	Fixed charges	82.69	64.56	62.06
	Production cost:—	287.79	239.13	246.52

specialists abroad. The process route closely follows the lines on which the massive, light fuel intensive ammonia plants have been built. They can be engineered on identical lines provided sufficient supplies of essential feedstock and fuel are ensured at one spot. There is a saving in first investment in comparison to low temperature fractionation technique. The cost of production of ammonia is also lower than for the latter provided the supplementary carbon dioxide recovery unit is avoided.

The third scheme discussed is suited for a case where coke oven gas availability may be limited, while blast furnace gas is plentiful and urea is desired as the end-product necessitating a supplementary source of carbon dioxide. On equipment side the scheme has almost same features as the previous one discussed. Investment savings are there probably due to fuller utilization of feed gases for synthesis mixture production. The operating cost may, however, represent a slightly higher figure than the previous one, though part of this should logically be attributed to carbon dioxide also besides ammonia.

Conclusion

In the present context, where a cheap fertilizer is the crying need of the day and a premium is put on a feed-

TABLE 3A—CONSUMPTION AND PRODUCTION

Basic Capacity—600 te/day Ammonia

Sl. No.	*Items*	*Alternative I*		*Alternative II*		*Alternative III*	
		Per te of Ammonia	*Per hr*	*Per te of Ammonia*	*Per hr*	*Per te of Ammonia*	*Per hr*
1.	Coke oven gas, Nm³ (in equivalent 10⁶ Kcal.)						
	(*a*) For Process	3810 (18.69)	95100 (466.0)	1412 (6.92)	35300 (173.0)	1062 (5.19)	26550 (129.5)
	(*b*) For underfiring	—	—	341 (1.67)	8515 (41.7)	—	—
2.	Blast Furnace gas, Nm³ (10⁶ Kcal.)						
	(*a*) For process	—	—	—	—	1302 (1.138)	32650 (28.4)
	(*b*) For underfiring	—	—	—	—	2880 (2.508)	72000 (62.6)
3.	Methane Fraction returned, Nm³ (10⁶Kcal) ..	1370 (11.15)	34225 (268.3)	—	—	—	—
4.	Rest gas returned, Nm³ (10⁶ Kcal) ..	180 (0.287)	4500 (7.17)	—	—	—	—
5.	Steam, te (—denotes exportable surplus)						
	(*a*) M. P.	—	—	−0.20	−5.00	−0.056	−1.40
	(*b*) L. P.	0.194	4.85	1.02	−25.50	−0.402	−10.03
6.	Electricity, kWh	1491	37250	1092	27310	1091	27280
7.	Process water, M³ make-up	17.9	447.0	17.0	425.0	18.65	465.5
8.	Boiler feed water, M³	2.3	57.5	2.18	54.5	2.25	56.25
9.	Ammonia production, te	—	25.00	—	25.00	—	25.00
10.	Carbon dioxide available, Nm³ ..	—	—	565	14125	945	23600

stock which can give cheapest ammonia, coke oven gas is a potential raw material which has not been fully exploited. From a steel complex's point of view, the modern trend is to plan for a comprehensive use of all energy resources from feed material to secure lower costs. Metallurgical coal especially has tended to claim a substantial part of the cost of the steel. In steel manufacturing schemes therefore, the tendency has been to cut down on coke consumption and shift emphasis to derived fuels like coke oven gas or lean gas to recycle heat to the process. In the net result, both carbonization capacities required as well as surplus coke oven gas available from integrated schemes have tended to dwindle. Even then from the national point of view, it should be possible to release this valuable by-product for fertilizer production by trying to rearrange the fuel utilization pattern substituting lean fuel for coke oven gas wherever practicable. F.C.I. has tried to popularize this idea by sponsoring schemes for fertilizer units as adjuncts to steelworks, pig iron complexes, merchant coke ovens, etc. Coke oven gas, unlike naphtha, is an indigenous feedstock. If quantitative production of nitrogenous fertilizers has to be achieved concomitantly with economy in cost, coke oven gas should be allowed to figure more prominently as a feedstock for fertilizer production.

Packaging of Fertilizers*

By

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Many of the fertilizers are hygroscopic and need protection from ambient humidity. Prevalent practice is to pack such fertilizers in moisture-proof bags. Multiwall paper bags with one or two moisture-proof plies have been in extensive use in the Western countries. In recent years all-polythene bags are becoming increasingly popular and steadily replacing multiwall paper bags. Such bags are prone to bursting or puncture unless proper care is taken during their handling. Rough handling under existing Indian conditions is a factor which goes against the wide use of such bags in India. Storage trial test results showed the superiority of polythene-lined jute bags over the other types. The thin polythene film is found to survive the stresses involved during handling, provided it is stuck to the jute with an adhesive. At present bitumen is used for this purpose. Polythene bags, however, can be tried as an experimental measure in a restricted way and assessment made of damage rates, types of failure and methods of despatch before final choice is made.

Many of the fertilizers, such as calcium ammonium nitrate, nitro-phosphates, urea, ammonium sulphate-nitrate and almost all of the multi-nutrient mixtures, absorb moisture from air at relatively low humidity and are referred to as hygroscopic materials. Such fertilizers when exposed to the atmosphere become moist and lose their free-flowing property. Drop in atmospheric humidity or temperature causes recrystallization of the soluble phase, inter-linking the particles together and causing the material to cake. The cake becomes hard on account of pressure during storage and considerable time and labour is wasted in breaking the caked material to a suitable size for application in the fields. When inadequately protected, hygroscopic fertilizers on prolonged storage suffer considerable loss of nutrient. To prevent this the normal practice is to pack such fertilizers in moisture-proof bags. Fertilizers, like mono-ammonium phosphate, potassium sulphate and potassium nitrate, pick up moisture from air only at a very high relative humidity and, therefore, do not require moisture-proof bags. Ammonium sulphate and potassium chloride fall on the borderline and employment of moisture-proof bags becomes necessary only in countries or regions that are highly humid. A few of the fertilizers like single superphosphate and triple superphosphate possess residual acidity and these

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require acid-resistant bags. Relative hygroscopicity of various substances are conveniently designated by their critical relative humidity which is the ratio expressed as a percentage of vapour pressure of the saturated solution to the vapour pressure of saturated air at the same temperature. A substance would absorb moisture only when the relative humidity of the atmosphere exceeds the critical relative humidity of the substance. Critical relative humidity values of most of the fertilizers and their binary mixtures are known (Table. 1).

TABLE 1—CRITICAL RELATIVE HUMIDITIES OF FERTILIZER SALTS AND BINARY MIXTURES AT 30°C, %

	Ammonium nitrate	Urea	Ammonium chloride	Ammonium sulphate	Potassium chloride	Potassium nitrate	Monoammonium phosphate	Monocal. phosphate	Potassium sulphate
Ammonium nitrate	59.4								
Urea	18.1	72.5							
Ammonium chloride	51.4	57.9	77.2						
Ammonium sulphate	62.3	56.4	71.3	79.2					
Potassium chloride	67.9	60.3	73.5	71.3	84.0				
Potassium nitrate	59.9	65.2	67.9	69.2	78.6	90.5			
Monoammonium phosphate	58.0	65.2	—	75.8	72.8	59.8	91.6		
Monocal. phosphate	52.8	65.1	73.9	87.7	—	87.8	88.8	93.6	
Potassium sulphate	69.2	71.5	71.3	81.4	—	87.8	79	—	96.3

[Most of the Data from *Fertilizer Technology and Resources in United States* by K. D. Jacob (Ed.), (Acad. Press Inc., New York), 1953]

World Trend

(*i*) *Multiwall Paper Bags:* The most common bags used for fertilizers that have dominated the scene for years are multiwall paper bags. Paper by itself is not impermeable to moisture. Holes, both of macroscopic and microscopic dimensions, exist in paper through which diffusion of moisture occurs with relative ease. A thin layer of bitumen blocks these holes and thus improves considerably the moisture barrier properties of paper. The moisture-proof bags of multiwall paper type consist of three to six plies of paper with one or two layers of bitumen between them. Varying degree of moisture protection is afforded by changing the number of moisture barrier plies. The kraft paper used now-a-days is of special quality possessing considerable wet-strength and is extensible and hence yields rather than cracks under rapid stresses. Entire quantities of hygroscopic fertilizers produced in U.S.S.R., W. Germany, Belgium and Sweden are bagged in such type of bags. In the U.S.A., U.K., France and Canada all plastic polythene bags are gradually replacing multiwall paper bags. In Italy, p.v.c. bags are widely used because of readily available chlorine. Reduction in the efficiency and strength of multiwall paper bags due to dehydration of paper and creasing are the chief drawbacks.

(*ii*) *All-Polythene or P.V.C. Bags:* All-polythene or p.v.c. bags are highly resistant to both water vapour penetration and residual acidity present in some of the fertilizers. High tensile strength and high stretch characteristics of these polymers make them survive certain amount of rough handling. Strength as well as puncture resistance of polythene film depend on its thickness. The stress to a bag involved during handling depends on the quantity of fertilizer put in it. For 50 kg of fertilizer, a film of 0.20 mm (8 thou) thickness is generally found to be satisfactory. Reduced thickness of 6 thou has been used for 23 kg of fertilizer. Open mouth bags require sealing. This is avoided by using valve-type bags which are slightly more expensive but not completely moisture-proof. In general, costs of polythene bags are 10-15 per cent higher than multiwall paper bags containing two moisture barrier plies. Notwithstanding the rising popularity of all-polythene bags, there are the following disadvantages associated with these bags in comparison to the multiwall paper bags. These objectionable features are of greater relevance as far as India is concerned.

1. *Puncture Proneness:* These are more susceptible to puncture. Care should be taken to see that the bags do not come in direct contact with project bolts, angle irons and wooden splinters any time during their handling. They also tend to be abraded on rusty iron chutes or warp themselves round roller conveyors if the space between rollers is excessive.
2. *Deformity Due to Stress:* Polythene being a visco-elastic material, certain amount of permanent deformation occurs when the bags are dropped from the shoulder height and the film becomes thin at places and develops weak spots which are liable to get punctured.

3. *Manual Handling:* It is not advisable to drag the plastic bags across the floor or the lorry bed by holding the corners but should be lifted and carried with arms around the bags.
4. *Stacking Problem:* These bags, because of low coefficient of friction are unstable during stacking and greater care is needed.
5. *Sealing Operation:* Heat sealing requires greater attention and is seldom trouble-free. Recently, hot air sealing has been introduced and found to be relatively trouble-free.

There is yet another point worth mentioning. Fertilizers stored in all-plastic bags are air-tight and equilibrium is attained between the moisture in the product and the air locked in the bag. Any drop in temperature, as it usually occurs between day and night, induces condensation of water vapour and the formation of saturated solution film on the granules and further decrease in temperature knits the granules together and the fertilizer cakes. This process of repeated crystallization and dissolution affects adversely the keeping quality of the product. Some of the plastic bag manufacturers provide vent holes for the fertilizer to breathe. This nullifies to some extent moisture-proofness of the bag. These are the reasons on account of which some of the leading manufacturers of both USA and U.K. are reluctant to switch over to polythene bags.

Serious attempts, however, are being made to remove the above defects. Increase in the stiffness of polythene film to facilitate ease of handling has been achieved to some extent by increasing slightly polymer density without making the film brittle. Recently, it has been reported that two or three films of polythene with varying density when used together overcome some of the defects mentioned above. Kraft paper manufacturers have come out with three-ply polythene coated extensible kraft sacks. It has recently been shown that free films of polythene in between multiwall paper plies are superior to polythene coated paper bags as far as moisture impermeability is concerned.

Our Experience

The problem of packaging of hygroscopic fertilizers was taken up at Sindri in 1957 before hygroscopic fertilizers viz., urea and ammonium sulphate-nitrate went into production. Till that time our experience in the field of packaging was limited to relatively less hygroscopic ammonium sulphate for which unlined jute proved adequate. The imported hygroscopic fertilizer tended towards "over packaging" which is understandable as it has to survive severe strain involved on account of rough handling at a number of places during its transit. At that time suitable indigenous bags were not available and we managed to procure from various sources different types of bags, viz. (a) multiwall paper, (b) p.v.c. coated jute, (c) kraft paper bonded to jute with bitumen and (d) polythene films of various thickness attached with or without bitumen to jute, for storage trial and performance evaluation tests. Results indicated superiority of polythene-lined jute bags over multiwall paper bags in the context of the adverse handling conditions prevalent in this country. Other types of bags did not possess sufficient moisture impermeability.

The above choice is justifiable for following reasons: (1) severe strain to which bags are subjected on account of manual handling—dropping from shoulder height and holding by ears of the bag is common practice; (2) absence of proper storage facilities for the bagged product; and (c) delays caused on account of transport bottlenecks before it reaches the consumers. The choice of bags depends on proper balancing of the protection it gives to the fertilizer against humidity, its ability to survive rough handling and cost.

The price of polythene film depends on its thickness. Therefore our attempt was to reduce the thickness of the film as far as possible. The results indicated that the optimum thickness was 0.05 mm (2 thou), provided it was laminated to jute with bitumen. Thinner liner did not provide adequate protection because the film is seldom uniform and variation in its thickness to the extent of 10-20 per cent have been noticed, and places where film is thin constitute weak spots which rupture on account of pressure from sharp edges of the fertilizers. One has to take this factor into account before arriving at the optimum thickness of the film. Moreover thinner liners tended to snap near the stitches.

Moisture barrier properties of bitumen are negligible in comparison to polythene film. The role of bitumen is solely that of an adhesive and keeps the film and jute bag together. This avoids folding up of the film during filling up and pressure from the fertilizers is directed uniformly on the outer jute bag. Heavy application of bitumen should be avoided as this causes embrittlement of liner on long storage. Polythene probably is not completely immune to the action of higher hydrocarbons. Moreover, experience shows that heavy application of bitumen leads to the necessity of frequent replacement of needles of stitching machines. No adhesive is required if the thickness of the film is increased. There are disadvantages to the use of bitumen, its foul smell being one of them. Moreover it reduces

the utility of empty bags for keeping grains or flour. An alternative is the hot-pressed lamination of plastic film with jute. In such bags, fibres of jute get embedded in the polythene film during extrusion and thus decrease moisture barrier properties of the film. There is a patented process in which polythene powder is used as an adhesive for sticking polythene film to jute. After being filled the bags are then stitched. This has its disadvantage as some amount of moisture is able to diffuse through the stitch holes of the final stitches. This did not occur on the side and bottom of the bag which were stitched with double lock stitches with seams folded. Absorption of moisture through the stitch holes is greatly minimized by stitching the filled bags on folded seams. Alternatively, the polythene film (in the form of the bag) is loosely inserted in the outer jute bag and then heat sealed or tied with a chord after filling it with fertilizer. The outer jute bag is then finally stitched. This practice is adopted at some places and is preferable provided the film is of sufficient thickness. Otherwise the film gets damaged during handling.

Jute overbag imparts the strength to the bag without making any contribution towards moisture impermeability. It is of utmost importance that the quality of jute should be such as is capable of withstanding rough handling. Jute should also be of close weave so that protruding nails or any hard projection do not come in direct contact with the thinner liner and at the same time the cost should be minimum. Jute mills produce a number of standard constructions suitable for bag making with every conceivable combinations of width, weight and count with varying quality of jute. Jute materials normally employed for sack making are as follows: (1) Twill sack (A Twill, L Twill, B Twill, etc.); (2) Tarpaulin; (3) Plane double warp bags (Heavy and light cees, D.W. Flour, etc.); and (4) Hessian—a plain fabric.

The price of different types of jute bags vary roughly in proportion to the weight and quality of jute and so does their ability to withstand rough handling. Considerable price fluctuations are a normal feature in the jute market and close watch by consumers on price trend is desirable. Twills, D.W. Tarpaulin, Cropped and Mangled Hessian types of jute have proved satisfactory.

In India the prevalent practice is to go in for bags each capable of holding 50 kg of hygroscopic fertilizers. Once optimum free space between the bulk of the fertilizer and stitches are fixed, the dimensions of the bag can be laid down after taking into consideration the bulk density of the fertilizer to be bagged and optimum length/breadth ratio. Ratio of length/breadth of 1.6 to 1.8 and a free space of about 4 inches are desirable for convenience in stitching, handling and stacking of bags. The stability of the bag is affected by any drastic change in the length/breadth ratio. This is important as the filled bag normally travels unsupported in a vertical position from the filling hopper to the stitching machine and finally to the loading chute.

Future Trend

With greater care and control over handling of bagged fertilizers as well as the improvement in the strength of all-plastic bags, it may be possible in future to go in for such bags. As an experimental measure these bags can be used in a restricted way. Then an assessment can be made of damage rates, types of failure and methods of despatch before a final choice is made.

The future of multiwall paper bags made from stretchable kraft paper of reduced capacity (25 kg) appears to be equally promising and may well in future provide answer to our packaging problem. Reduction in the capacity of the bag from 50 to 25 kg will minimize strain on the bag and remove some of the handling problems. Furthermore, bags of reduced capacity may in fact find favour with consumers. As such types of bags are not available indigenously, it is difficult to predict their cost. The same is true of all-polythene bags although one of the intending manufacturers indicated the price of such bag of 8 thou thickness to be close to the existing price of polythene-lined jute bags. But one does not find any reason why multiwall paper bags may not turn out to be cheaper and effective packaging material for hygroscopic fertilizers in India.

While presenting the paper, the author had the following comments to make: The problem facing the packaging technology involves the choice and design of bag that would provide adequate protection with minimum cost. At the moment, the price of moisture-proof bag used for 50 kg of fertilizers like urea, ammonium sulphate-nitrate and calcium ammonium nitrate is around Rs. 160.00 per 100 bags. Jute and polythene films constitute roughly 65 and 25 per cent of the total cost of the bag respectively. Any significant reduction in the cost of the bag is possible only if the price of jute and/or polythene comes down. The possibility of jute becoming cheaper appears to be unlikely. Polythene may become cheaper when it is produced from petroleum sources rather than from alcohol, which is the source at the moment. Savings have, however, been achieved by trying out inferior variety of jute and

thinner gauge of polythene. Nevertheless, one has to be careful as, at the moment, ours is a seller's market and we are prone to overdo economization at the cost of quality of product.

As regards packaging of superphosphate, here too polythene-lined jute bags have proved a success though the purpose for which polythene is used is to protect the jute from the attack by acids such as phosphoric and fluosilicic acids. Cured superphosphate containing low acid/water ratio is non-hygroscopic.

Lastly about the future of multiwall paper sacks in India. With the advent of extensible or stretchable kraft papers, the future of multiwall paper sacks is bright. Moisture barrier plies may be of bitumen for less hygroscopic product and thin film of polythene for more hygroscopic ones. Such a bag will be more flexible, and the desired degree of protection can be given to fertilizer keeping in view the keeping quality of the product and the ambient conditions of humidity and temperature of the region served by the fertilizer.

Ammonia Loss During Storage of Calcium Ammonium Nitrate: Role of Calcium Nitrate

By

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The effect of calcium nitrate on the liberation of ammonia from CAN has been studied. Calcium nitrate is found to inhibit loss of ammonia. The extent of inhibition is dependent on Ca $(NO_3)_2/H_2O$ ratio, the value of which varies if the diluent is a reactive limestone or pure chalk. Limestones tend to be more reactive than pure chalk.

In a previous communication,[1] it was pointed out that calcium nitrate present in calcium ammonium nitrate has a retarding influence on the evolution of ammonia during storage of CAN in silo and the extent of inhibition may be dependent on calcium nitrate/water ratio—higher the ratio lesser will be the loss. This is important as calcium nitrate is invariably present in CAN and the above ratio increases perceptibly during storage of the fertilizer.

In the present work, the effect of calcium nitrate on liberation of ammonia has been studied. Samples containing varying ratios of Ca $(NO_3)_2/H_2O$ is taken by varying the proportion of calcium nitrate in the same amount of water, i.e. 10 ml. These samples are then saturated with ammonium nitrate. Small quantity (lg.) of limestone/chalk is then added. Ammonia evolution is detected by smell and pH paper. pH of the samples is then determined. pH of a saturated solution of ammonium nitrate is around 4.6, while the same of an aqueous limestone or chalk is 9-9.1. When both ammonium nitrate and limestone/chalk are together, the resultant pH is about 6.85 (pH of CO_2-free water 6.9).

The graph (Fig. 1) of pH vs Ca $(NO_3)/H_2O$ ratio is drawn for three varieties of limestone (one of which, sample 4, gave high aqueous alkalinity). Addition of limestone/chalk to the saturated solution of ammonium nitrate caused evolution of ammonia, which could easily be detected by smell and pH paper. The sudden drop in pH of the mixture between the Ca $(NO_3)_2/H_2O$ ratios 0 to 0.1 and 0.1 to 0.5 is attributed to the inhibition of hydrolysis of calcium carbonate and consequent decrease in the evolution of ammonia, since aqueous calcium nitrate is only slightly acidic (pH 5.9) and that any increase in the concentration of calcium nitrate in the mixture is found to decrease pH in a regular way simulating the lower portion of the curves, i.e. between the $Ca(NO_3)_2/H_2O$ ratio 0.75 to 1.25 in the case of pure $CaCO_3$ (Fig. 1).

Ammonia liberation decreases as the calcium nitrate content is increased and a stage is reached when there is no smell of ammonia nor its presence shown by the pH paper. At this stage the $Ca(NO_3)_2/H_2O$ ratio is shown by arrows (Fig. 1). It is evident from the graph

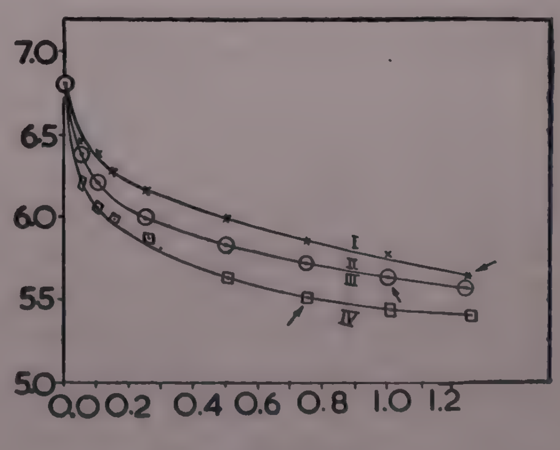

Fig. 1—pH vs. Calcium Nitrate/Water Ratio.

Sample I—Limestone (Rishikesh)
Sample II—Limestone (Jharbeda)
Sample III—Limestone (Himalaya & Co.)
Sample IV—Pure chalk

The curve for sample III is overlapping on the curve of sample II. Ratio at which there is no indication of ammonia evolution is shown by arrows.

that optimum ratio of $Ca(NO_3)_2/H_2O$ at which ammonia is undetectable in the case of pure chalk (sample 4) is 0.75 and for the reactive limestone the value is 1.25 (sample 1). For the other two limestones the value is 1.0 This shows that more calcium nitrate is required to inhibit the evolution of ammonia in the case of reactive limestone. In other words, CAN with this limestone as diluent will continue to liberate ammonia till the optimum $Ca(NO_3)_2/H_2O$ ratio is reached, the value of which is higher than when other varieties of limestone are used. This difference is less prominent when the moisture is low or extremely high.

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A Method for Estimation of Polyphosphate in Cooling Waters Containing Dissolved Chromate

By

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A method has been developed for estimation of polyphosphate in cooling waters containing dissolved chromate. It consists in separating out the orthophosphate, both initial and that formed from polyphosphate after acid hydrolysis, from chromate by the addition of alum, ammonium chloride and ammonia to the water. The orthophosphate in the precipitate is estimated by the usual colorimetric method and the polyphosphate content is obtained by the difference between the orthophosphate formed after hydrolysis and that present initially.

A mixture of chromate and polyphosphate in suitable proportions is added in cooling waters in many places to prevent corrosion and scale formation. In a previous communication[1], results were reported on the effect of chromate-polyphosphate combination in inhibiting corrosion of mild steel, brass and admiralty metal in cooling waters. Because of the presence of chromate, usual colorimetric method for the estimation of polyphosphate in these waters is not satisfactory, even with the addition of reducing agents. In the present study, a method has been developed for accurate estimation of polyphosphate in cooling water in presence of chromate.

The method consists in separating the orthophosphate, initially present in water, by precipitation with alum and estimating it colorimetrically[2] in the precipitate. The polyphosphate present is next converted into orthophosphate by hydrolysis and the total phosphate is estimated in a similar manner. The difference between the two values gives polyphosphate content in water.

Procedure

A. *Orthophosphate Content:*

To 50 ml. of the cooling tower water treated with polyphosphate and chromate is added 0.5 g. of ammonium chloride and 1 g. of potash alum. (The quantities may be adjusted according to the phosphate content in water). Ammonium hydroxide is then added with stirring until the solution is alkaline and then it is allowed to stand for 15 minutes. The precipitate obtained is filtered through Whatman No. 42 filter paper and washed with cold water till free from chromate. The residue is dissolved in the minimum amount of sulphuric acid (dil.) and made up to 100 ml. An aliquot of this solution is taken for colorimetric estimation.

To an aliquot of the above solution, a drop of phenolphthalein is added and then ammonium hydroxide is added drop by drop till a pink colour appears; rest of the procedure is the same as that followed in the standard colorimetric method[2].

B. *Total Phosphate:*

To 50 ml. of the same cooling water sample as in A is added 5 ml. sulphuric acid (1 : 2). The solution is boiled for one hour on the hot plate, distilled water being intermittently added to keep the volume to about 25 ml. About 3 g. of potash alum is then added, the solution cooled to room temperature and a drop of phenolphathalein indicator and 1 g. of ammonium chloride are added. Ammonium hydroxide is next added dropwise till the solution is alkaline, and the solution is boiled for 15 minutes and then allowed to stand for further 15 minutes. The precipitate is filtered through a Whatman No. 42 filter paper and the residue is washed several times with hot water till free from chromate. The residue is dissolved in minimum amount of sulphuric acid (dil.) and made up to 100 ml. An aliquot of the above solution is taken for colorimetric analysis as in A.

The amount of polyphosphate in water is obtained by subtracting the PO_4 estimated in A from that in B.

Results and Discussion

In Table 1 are given the results of estimation of polyphosphate in absence of chromate in samples of water by the standard method and also by the method evolved in the present study. There is complete agreement between the two sets of values.

In order to test the applicability of the new method in presence of chromate, known amounts of polyphosphate and chromate were added to water samples and the polyphosphate was estimated by the method.

In Table 2 are given the results of studies in which known amounts of chromate and polyphosphate were added to water and the latter estimated by the new method. It will be observed that the experimentally determined values agree with the calculated ones.

TABLE 1—ESTIMATION OF POLYPHOSPHATE IN ABSENCE OF CHROMATE, *mg*.

(Values represent average of six readings.)

Polyphosphate by usual method, as PO_4	*Polyphosphate by the new method, as PO_4*
0.32	0.32
0.22	0.22
0.72	0.72

TABLE 2—ESTIMATION OF POLYPHOSPHATE IN PRESENCE OF CHROMATE, *mg*.

(Values represent average of six readings.)

By the new method, as PO_4	*Calculated as PO_4*
0.32	0.32
0.32	0.32
0.22	0.22

The authors wish to thank Dr. K. R. Chakravorty, General Manager, for his interest in this work.

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Pilot Plants

Production of Ammonium Bicarbonate at Sindri

At present 4,000-5,000 tonnes of ammonium bicarbonate are needed annually in our country mainly for use as baking powder and also in smaller quantities in rubber and pharmaceutical industries amounting to an expenditure of Rs. 18 to Rs. 22 lakhs in foreign exchange.

A Section of Ammonium Bicarbonate Plant Showing the Dryer (right foreground).

Considering the facilities available at Sindri, the Planning and Development Division of FCI Ltd., took up studies for the production of this chemical, and after extensive laboratory investigations set up a pilot plant of ammonium bicarbonate with a capacity of 0.5 te/day. Based on the successful results obtained in the pilot plant tests, a bigger plant was indigenously set up with a capacity of 4.5 te/day, i.e. 1,400 te/year. The plant has been in operation since April 1965 and by the end of December 1965 produced 700 tonnes of ammonium bicarbonate. The target for 1965-66 is 1,000 te and this will save Rs. 5 lakhs in the foreign exchange. With regular production in this plant, a foreign exchange saving of about Rs. 6.5 lakhs is expected, and the value of the product will be Rs. 12-13 lakhs. Plans are being made to increase the capacity to about 30 te/day.

The quality of the product manufactured conforms to the specifications laid down by Indian Standards Institution to be used in the food and pharmaceutical industries.

Steam-Naphtha Reformation Plant

Gasification of petroleum feedstocks by catalytic steam reforming is the latest and cheapest method of obtaining synthesis gas for manufacture of ammonia, methanol, etc. The catalytic steam-reforming process using indigenously available surplus naphtha has a great potential in India. The Planning and Development Division of FCI Ltd. has initiated studies on the development of the above process.

After successful completion of laboratory-scale studies, a small pilot scale pressure naphtha-steam reformation plant has been departmentally designed, fabricated, installed and finally commissioned. The plant is meant for obtaining technical process design and development data and also for developing a suitable catalyst for the process. The preliminary trial run has been quite successful and encouraging results have been obtained.

Hydrotreatment of Naphtha

Naphtha obtained from the Indian refineries contains sulphur in the form of organic sulphur compounds. The tolerance for sulphur by the nickel-based catalyst in the steam-reforming of naphtha is of the order of 5-8 ppm. So the removal of sulphur by, say, catalytic hydrotreatment of naphtha is an essential pretreatment prior to steam-reforming.

After successfully completing laboratory-scale studies on hydrodesulphurization of petroleum feedstocks, a small-scale pilot plant on the hydrotreatment of naphtha at elevated pressure has been designed, fabricated and installed departmentally.

Notes & News

Process Know-How on Urea Manufacture

The Fertilizer Corporation of India has entered into an agreement with Montecatini of Italy on Jan. 22, 1966. for the purchase of Fauser-Montecatini process for the manufacture of urea.

In the total recycle Fauser-Montecatini process, carbon dioxide and ammonia are reacted at a pressure of 180-200 kg/cm^2 in presence of excess ammonia. The unreacted raw materials are completely recycled. The recovery of unreacted materials is carried out in two steps at 25-35 kg/cm^2 and at about 1 kg/cm^2. The urea solution after the removal of unreacted material is concentrated to 99.5 per cent in two stages viz. at atmospheric pressure and under vacuum. The melt is then prilled, cooled and sized. FCI has obtained a non-exclusive right to exploit this process to build fertilizer plants.

Montecatini will make available to FCI all technical know-how and design data essential for carrying out the engineering design and drafting of the plant. Also, Montecatini will allow a reasonable number of FCI engineers to work in the Montecatini office at Milan, Italy, for a certain period of time to acquaint them with the basis and methods of process design calculations.

The engineering design of the plant on the basis of process design will be done completely by FCI engineers. However, if FCI so desires, those designs will be checked by Montecatini engineers. Montecatini will fully guarantee about the capacity and specific consumption figures for the plant.

Under this agreement, FCI is now building two plants—one at Durgapur for FCI and another at Cochin for Fertilizers & Chemicals, Travancore (FACT)). The capacity of each plant will be 1000 te/day unprilled urea and will be laid out in two streams.

Gas Hazards in Industry

Under the auspices of the Safety First Association of India (Bihar Branch), a seminar on Gas Hazards in Industry was held in the Training Centre, Sindri on February 14 and 15 under the chairmanship of Sri A. N. Singh, Chief Inspector Factories, Bihar, with the Sindri Unit of FCI Ltd., playing the host. Over 60 delegates attended the seminar, and in all 6 papers were read and discussed out of which the following were from this Division: (i) 'Detection and Estimation of Traces of Carbon Monoxide in Atmospheric Air and Gas Samples by Gas Chromatography' by A. Sinha and S. K. Ghosh: (ii) 'Explosion Control by Materials Evaluation' by K. C. Banerji.

While inaugurating the seminar, Sri K. C. Sharma, General Manager, Sindri Unit, said that the fertilizer industry has its own problem of gas hazards viz. toxicity, explosivity, etc. There is hardly a gas which did not have dangerous characteristics associated with it, and even an inert gas like nitrogen is poisonous under certain conditions. It is a highly technical matter to foresee and control the dangerous reactions of gases.

Sri A. N. Singh in his address emphasized the need for training in safety, especially in gas hazards even purely on economic considerations. The country is losing lakhs of rupees through accidents due to gas hazards. Of course it has yet to face with accident problem outside the industry like in the USA, where there is more loss of life due to accidents caused outside the factories.

Carbon monoxide is a very common gas in fertilizer industry. Its hazards in causing poisoning and explosions are too well-known, for which a maximum safe limit of 100 ppm in factory premises has been specified under statutory regulations (Sindri factory has prescribed a maximum limit of 50 ppm). The quick detection of carbon monoxide as required under safety regulations has hitherto been carried out by CO-detection tubes which used to be imported. Its non-availability now has posed a serious problem. Dr. A. Sinha and Sri S. K. Ghosh claimed to have developed an accurate gas chromatographic method for quick detection and estimation of carbon monoxide.

Many of the failures in chemical plants, including those at the FCI, result from a variety of causes starting from manufacturing defects of the material of construction, errors in design calculations upto variations in the specified operation condition beyond the permissible limits. In his paper, Sri K. C. Banerji has enumerated various defects responsible for causing failures and explosions in chemical industry which can be broadly classified into 3 groups, viz. (i) inherent defects or the metallurgical defects introduced during the production of the base material, (ii) processing defects introduced during fabrication of the particular equipment and (iii) service defects introduced during the operating cycle of the equipment. Non-destructive testing techniques have now reached such a perfection that they permit a reasonably accurate assessment of the conditions of plant equipment, both its metallurgical as well as surface conditions, so that a reliability factor can be worked out for the plant's safe operation within the period of its designed life. Among the NDT techniques, the following may be distinguished: (a) radiography, (b) ultrasonic transmission and resonance, (c) magnetography and other magnetic techniques and (d) electric induction. The explosion in the high pressure line of ammonia synthesis section at Sindri (Oct. 1963), caused due to corrosion-erosion, could have been prevented by periodic checks and employing the above techniques. Ultrasonic methods coupled with radiographic density evaluation helped to detect the extent of hazards involved in continuation of the cracks in a CO_2 scrubber at Sindri.

Among other papers, there was one from the Sindri Unit, wherein the author, Dr. S. Vedaraman, has dealt with case studies of some of the recent explosions in ammonia plants in India. The explosion

in the ammonia synthesis unit no. 2 of the Sindri Unit, which took place on 21.10.63, was caused by a sudden failure of a high pressure pipe bend from the cold exchanger to the secondary condenser. This failure resulted in a sudden release of gas under high pressure almost instantaneously followed by extensive fire caused by the high pressure synthesis gas mixture gushing out at a high velocity and burning itself. An examination of the pipe showed that the walls had thinned down considerably as a result of erosion.

Development in TVA

Two new products viz., 11-37-0 base solution and 12-40-0 base suspension, produced recently by the Tennessee Valley Authority are being widely used by manufacturers of U.S.A. Sodium ammonium phosphate nitrate and granular high-analysis phosphate were introduced in different states. The places which are deficient in sulphur are using ammonium nitrate sulphate.

TVA's concentrated superphosphate is being used by a firm for manufacturing 1,900 tons of grades 0-20-20 and 5-20-20 to be used in the county forage fertility programme. In 1963, mixed fertilizers manufactured by the TVA materials averaged 47.7% plant nutrient content with the state average of 32.8% for all mixtures. Two larger of TVA materials, one containing 11-37-0 base liquid and the other ammonium phosphate nitrate (30-10-0), were supplied to Nebraska to improve the farm operations at reduced cost.

Research and Development: Research work is being continued on the synthesis of formamide and coating of conventional nitrogen fertilizers to slow their rate of dissolution. To reduce the costly losses of nitrogen of the compounds to the air and to drainage water, during the growing season, study on oxamide was continued. Isotope N^{15} is being used for nitrogen investigation with the help of a mass spectrometer.

Information on the measurements of the heat liberated in the acid-ammonia reaction obtained during the production of ammonium polyphosphate fertilizer (15-61-0) is being utilized for design calculations for constructing a granular fertilizer unit.

A new simplified process has been developed to produce ammonium polyphosphate of about 12-58-0 grade from wet process phosphoric acid and the heat of the reaction is utilized to evaporate water from the acid. Efforts are being made for producing phosphoric acid by wet process of 40 or 50-55 per cent concentration instead of the 30 per cent resulting from conventional practice. Impurities, which precipitate out forming troublesome sludge in the set process phosphoric acid, are mostly complex iron and aluminium phosphates and small amounts of potassium.

Variation in mineral character of phosphate in different places may help to explain the different behaviour of chemically similar compounds during processing. From low cost ingredients, urea-ammonium phosphate combinations may be manufactured and can be used as a good fertilizer.

Pilot plant work with nitric phosphates was concentrated on reduction of the recyclo ratio which improved dryer efficiency and control of dust fumes.

Micronutrients: In simple and inexpensive ways, powdered micronutrients were added to bulk blended fertilizers which are being used. Addition of small amounts of water and oil to the blend causes the micronutrient to cling to the fertilizers.

Zinc oxide, zinc carbonate and zinc sulphide were added to solid fertilizers and they were less expensive but equally effective than zinc sulphate. Boron, copper, zinc, manganese and molybdenum were added to a liquid 11-37-0 solution which was successfully used to cold mix several fertilizer grades.

Process Improvement: TVA has developed some new techniques to recover more nitrogen from the pressure nitric acid unit by reducing the amounts of nitrogen oxides escaping to the atmosphere and installed a centrifugal to recover 95 per cent of the phosphorus from sludge an unavoidable residue in electric furnace production of high purity phosphorus.

[Phosphorus and Potassium No 17, June 1965]

Changing Trends in Fertilizer Industry in USA

Net income in farming in America has been $13 billion anually during the last 10 years and the average income per agricultural farm is on the rise. With the increase of farm production, the demand of the fertilizers is also on the rise. More emphasis is being laid by the industrialists on research work to improve the quality of fertilizer and its marketing and distribution systems. The farmers are taking keen interest in the technological advances of fertilizer industry. Time is approaching when the farmers will adopt the sophisticated techniques such as linear programming, weather service and crop forecasting for increase of production and for more profit.

The industrialists are investing more on the chemicals associated with the fertilizer industry. With the increased supply of low cost natural gas and applying some new techniques, it is possible to make 1000 tons/day ammonia plants attractive. If a cheaper nitric acid is available, nitrophos plants offer economies in both shipping and production. Efforts are being made to manufacture 80 per cent phosphoric through removal of water from regular 54 per cent acid obtained in the wet process manufacturing of phosphoric acid. In producing maximum yields of certain crops, sulphate of potassium is more useful than its chloride and so emphasis is being given to it. Plant growth demands the inclusion of micronutrients in definite proportions to various types of fertilizers. Excess of micronutrients may have toxic effect.

Research work is going on the possibility of slurry fertilizers and recovery of potassium forms from brines at lower cost such as by ion-exchange which is preferable to the expensive crystallization process. Slurries can be made with about 50 per cent more total nutrient content than liquids and they can be spread by specially designed slingers or modified spray nozzles used for liquid muds. Since the slurries are in the solution form they are quickly available to the plants.

IMC is currently working with a plant regulator—triiodobenzoic acid (TIBA) which has the ability to reduce vegetative growth in soya beans.

To know the problems of the customers "cluster" of smaller units are made around a mother plant. The distribution department embraces order processing, warehousing, material handling and the responsibility of co-ordinating closely with production scheduling. IMC has engaged 6000 cars to carry fertilizer products to meet the needs of the customers. The computers handle the problems regarding shipments and demand of the fertilizers.

A giant warehouse 50,000 for "bubble"

that will be in the Minneapolis area for storage of potash is a nylon and plastic structure which can be blown and supported completely by air pressure. It is complete with conveyors for loading and unloading. This can be simply collapsed and moved.

Overseas developments will also affect American fertilizer industry products, research planning, transportation, warehousing and other segments. Total world investment in N-P-K today is $ 3 billion and demand of 1980 will require investment of $ 14 billion.

[NPKS Abstracts 51 (1965), May]

Today's Ammonia Plants

Total world usage of nitrogen for fertilizers increased 600 per cent between 1930 and 1960 and was a major factor in enabling the means of subsistence to stay ahead of a geometrically expanding population. According to many predictions world population will exceed 5 billions by 1990—a two-third increase over 1960—and to prevent hunger by more farm production, the nitrogen usage for fertilizer must rise another 400 per cent from an annual 10 million tons in 1960 to 40 million tons in 1990.

To meet the growing demand of ammonia and for more profits, the ammonia makers of America are using new sophisticated techniques which can increase the operational efficency of the machines of the ammonia plant. Emphasis is being laid on the improvements of plant designs and location of the plant, and its size are taken into consideration to reduce the transportation and operating cost. Present plants are approaching 30×10^6 Btu per short ton with negligible power consumption as opposed to past plants which used 31×10^6 Btu and 850 kwh. per short ton.

Every major step in the ammonia flowsheet has changed in the past ten years. Indications are there for larger plants, highest possible reforming pressure results in the most economical plant which are technically feasible. Savings in increased heat recovery per unit increase in pressure are much lower at higher pressure. But the installation cost of pressure system has also to be borne in mind. Reforming was operated previously with a steam to carbon ratio of between 4 and 6 at 10-100 psi, while present steam/carbon ratios range between 3 and 5 at 200-600 psi.

CO-conversion design is a balance of temperature, steam consumption and catalyst quantity to arrive at the minimum CO level consistent with overall plant design. The most significant change in plant design is the use of low temperature CO-conversion catalyst which is active in range 400-600°F, allowing CO levels, perhaps one-tenth of those previously reached. CO-conversion, previously a two-stage operation with CO_2 removal between stages, is now one stage. Normal installations of the catalyst contain a renewal bed of zinc oxide to assure that the poisoning sulphur will be nil. Low temperature shift catalyst makes one-stage CO-conversion much more efficient. Efficient low temperature catalysts also minimize steam usage. Pressure has a marked effect on quantity of CO-conversion catalyst. A plant operating at 20 atm. require only 50 per cent of the catalyst necessary at 5 atm. Inerts are made up of argon from secondary air, residual methane from primary reforming, and residual CO and CO_2 that have been methanated after the CO-conversion and CO_2 removal steps. The CO exit conversion is the only one of these that can easily be changed so that there is less methane to the synthesis loop. By decreasing the levels of inerts, purge can be reduced to produce more ammonia. For CO_2 removal, hot carbonate, Catacarb, Vetrocoke and Sulfinol processes are employed for lower operating cost through less regeneration heat and corrosion values.

The less heat is used by CO_2 removal system, the more heat will be available for power recovery. In the Sulfinol process, CO_2 loading is as much as twice that of menoethanolamine (MEA) and heat duties and tower diametres are proportionally less. Final purification, classically done by copper liquor process, is now carried out by methanation over a nickel base catalyst.

Instead of using reciprocating machines operating to 10,000 or 15,000 psi for ammonia synthesis, current large plants have centrifugal machines for compression and synthesis recirculation, and the reaction pressure has been dropped to the range of 2,000 to 3,000 psi.

Synthesis loop now operating at 2000 to 3000 psi are using quench reactors exclusively to replace the tubular reactors used at higher pressure levels. Refrigeration levels have necessarily dropped to remove ammonia formed. Both of these changes are the result of centrifugal compressors.

In producing ammonia from the mixture of hydrogen and nitrogen, the equilibrium is favoured by a high operating pressure and low inert gas content. Although equilibrium is favoured by low temperature, converters are generally operated with a maximum catalyst temperature of about 500°C in order to obtain a satisfactory rate of reaction. A well designed plant will have balanced the cost of forming ammonia vs the cost of producing synthesis gas.

The larger the plant is, the more efficient it is because operation costs will decrease. But larger plants must service a large marketing area and the cost of transportation must be considered, and thus suitable location has to be selected to minimize such cost.

[Sydney A. Bresler and G. Russel James, Chem. Engng, 72 (1965), 13, 109]

Fertilizer Industry Round Table

In his opening remarks at the 14th annual meeting held in Washington D.C. on November 11-13, 1964, the Chairman, Mr. Vincent Sauchelli, emphasized that the aim of the Round Table sessions is for promoting the interest of the fertilizer industry and particularly of the men in it, like plant superintendents, the quality control staff, the foremen, the material handling and the maintenance personnel, who are directly engaged in the manufacturing function.

Packaging is an important factor for storing and transporting products to the consumers. The sack used for highly competitive fertilizer industry must provide maximum protection against moisture, acid and chemical vapours of certain grades, has to withstand adverse climatic and temperature conditions, be easily closed with either adhesives, thread or heat sealing, be tough and resistant to puncture and rough handling, should have an excellent get-up for market appeal and yet be economical.

There are three types of sacks used for packing and shipping fertilizers: (1) Multiwall paper sacks, (2) Heavy Duty Plastic sacks and (3) Plastic and Paper combination sacks. Paper bag is low in cost and yet strong, scratch resistant and handles and stacks well. But the main disadvantages are that they are permeable to acid and moisture.

Plastic bags are also of much use because they are also cheap and resistant

to moisture and acid attack. But plastic bags get punctured easily. A light-weight plastic bag which is wrapped with paper is most convenient and combines the advantages of the first two types of bags for many grades of fertilizer and fertilizer materials. This bag, though a bit costlier than either of the first two, is tough and strong and provides protection for the more hygroscopic nitrogen goods and superphosphate fertilizer. For various types of fertilizers, the following are the ways of bag constructions of paper and plastic combination. For packaging P—K goods and to resist the corrosive action of the gases flat tube sewn open mouth bag is manufactured. For this type, blown tubing ¼″ narrower than the paper walls can be used as the inside ply and if desired it can be heat-sealed. Next there is gusseted sewn open mouth type bag for which flat film is generally used for either the inside ply or for placement between plies for more moisture protection. The next is gusseted sewn valve which can be manufactured in the same way as the previous one and which can be heat-sealed at both ends. There are pasted valve bags to resist cold temperature below freezing.

Robert E. Szold in his paper has referred to nitrogen solutions containing 0.5 per cent maximum water as "dry nitrogen solutions", which have been introduced commercially in 1960 under name DRI-SOL. These provide one or more of the following benefits: better process control; increased rates; decreasing drying cost; improved product quality, etc.

Mr. John Harris gave a little about the new process known as 'SAI-R' for high concentrated granular fertilizer developed by the Scottish Agricultural Industries Ltd. In another paper he described a new form of ammonium phosphate (sold under registered trade mark PhoSAI). It has properties very similar to superphosphate and can be used directly as a replacement for superphosphate in TVA and conventional type of NPK granulation plant. It can be further ammoniated to various levels of diammonium phosphate content. John Frederick has described the modifications necessary to convert a typical TVA type granulator capable of producing ammonium phosphate of mixed grades so that part or all of the P_2O_5 is supplied by phosphoric acid (wet process) and part or all of the nitrogen is supplied by ammonia either from solutions or as anhydrous ammonia.

[Proceedings of the 14th Annual Meeting, Fertilizer Industry Round Table 1964]

News in Brief

Red Phosphorus as Fertilizer

Considering the factors of storage and transport, the modern trend in the fertilizer industry is towards more and more concentrated fertilizers. In the case of phosphorus fertilizers, the ultimate maximum concentration is the pure element itself. Of the three forms of phosphorus, the white is very poisonous and most reactive and the black is completely inert. Red phosphorus is non-poisonous and less reactive than white phosphorus and for these reasons can be only considered as a fertilizer among the three.

It has recently been found in New Zealand, by Dr. H. P. Rothabaun, that red phosphorus is slowly oxidized in soil, mainly to orthophosphoric and polyphosphoric acids, but also to some toxic acids. The non-toxic acids are valuable sources of phosphorus for plants. It has been found that addition of copper compounds accelerates the oxidation of the oxidized red phosphorus and so prevents the accumulation of toxic compounds. Copper increases the annual amount of red phosphorus oxidized.

Even in the presence of copper, red phosphorus is nevertheless a slow-acting source of phosphate—only about 20 per cent is oxidized a year. Where the phosphate level is satisfactory, phosphorus is applied to maintain this level and it is applied with a quickly acting phosphorus fertilizer such as superphosphate.

In either case, the red phosphorus will supply the soil with phosphate over a number of years.

[New Scientist, 29 (1966), No.478, 79]

Naphtha for Steam Reforming

The specification of naphtha to be used in India for steam reforming is broadly as follows: (1) It shall be straight run with a final boiling point upto 200°C. Naphthas of boiling point as high as 230°C can be accommodated by the process under special circumstances; (2) *Sulphur:* There is no firm limit set for the sulphur content and sulphur removal units are included in the plant so that the material entering the reformer contains no more than 5 ppm. The naphtha purchased at Billingham (by ICI in U.K.) contains a maximum of about 1000 ppm; (3) *Unsaturation:* ICI Agricultural Division has specified that a few per cent unsaturated components can be tolerated and the Power Gas Corpr. has mentioned a maximum of 10 per cent. Agricultural Division has shown that for gaseous feedstocks of C_3 and C_4 types the upper limit for olefines content is 20 per cent; (4) *Aromatics:* No upper limit has been set for the aromatics content of reformer feedstock. Agricultural Division has successfully reformed naphtha containing about 35 per cent aromatics.

[Circular Letter from Union Ministry of Petroleum and Chemicals, Govt. of India, March 8, 1966]

Performances of Sindri & Nangal Fertilizers Works

Sindri factory of the FCI Ltd. has established an all-time production record during the financial year 1965-66. Total nitrogen fixed in the end-products including sale of ammonia and nitric acid was 97,912 tonnes exceeding the target fixed for the year by 405 tonnes. Production of ammonia in the expansion plant was the highest ever achieved—39,631 tonnes, being 1004 tonnes higher than the previous record reached in 1962-63. Production of ammonium sulphate was 326,757 tonnes exceeding the target by 6757 tonnes while production of ammonium sulphate nitrate was 55,255 tonnes exceeding the target by 255 tonnes. Production of urea was 19,025 tonnes, exceeding the target by 1025 tonnes, which is an all-time record being 308 tonnes more than the previous highest figure of 18,717 tonnes achieved during 1962-63.

The Nangal Fertilizer and Heavy Water units have exceeded the revised targets for 1965-66 in respect of both calcium ammonium nitrate (CAN) and heavy water, the revised targets being CAN 336,450 tonnes and heavy water 8,907 Kg. Before the factory was shut down for annual maintenance and repairs from March 29, 1966 the actual production of CAN was 337,952 tonnes and of heavy water 8,912 Kg.

Packaging

Multiwall bags are being designed in such a way that they may withstand most of the shipping hazards, breakage, product loss and ultimate dissatisfaction of the customers. To resist slipping off stacks and papers that strech, bags are manufactured from impact resistant and friction finish papers. Stronger, more sift-proof closures, paper seals, sleeves, valves, inserts and other structural features have been incorporated into bags to increase strength, handling and filling ease, and protection of the contents. Ammonium phosphates 16-20-0, 13-90-0, 12-24-12 and 13-13-13 are among the least hygroscopic and therefore need less of a moisture-barrier bag.

The diammonium phosphates contain more nitrogen and therefore more hygroscopic, requiring more of a moisture barrier. The 18-46-0, 16-48-0, 12-36-12 and 14-28-14 mixtures are examples of this grade. Similarly heavier barrier sheets are needed in packaging the triple superphosphates.

The urea and ammonium nitrate grades have supplemental nitrogen added that cannot be derived from ammonia. Grades 30-15-0, 20-20-0, 15-15-15 and 33-5-0-0 need heavy barriers and in many cases a flat sewn open mouth bag is used employing a seamless polytube as the inner ply. The same type bag is used for refined potassium chloride.

Barriers are also required to combat the effects of acids in some fertilizers. For example, the combination of H_2SO_4 and phosphate rock may be such that there is an excessive amount of H_2SO_4 and/or H_3PO_4 both acids which could react with the bag and destroy the cellulose fibres in the paper. To minimize this problem, the barrier sheet should be the inside ply with the poly facing the product to combat the acid deterioration of the paper.

[NPKS Abstracts, 40 (1965), April 9]

Price of Fertilizers

Under notification from the Union Ministry of Food and Agriculture, Government of India, has fixed the maximum prices per tonne of the following fertilizers whether for the use of tea, coffee or rubber plantations in Kerala, Madras, Mysore, Assam or W. Bengal or for use of cultivators will be as follows: ammonium sulphate Rs. 405 and Rs. 416 when packed in 100 and 50 kg. bags respectively; ammonium sulphate nitrate Rs. 515; urea Rs. 680 and CAN Rs. 365.

[Deptt. of Agriculture, Union Ministry of Food & Agriculture Notification, Jan. 29, 1966]

Pool Issue Prices of Fertilizers

Under notification, the Union Ministry of Food & Agriculture, Government of India, has fixed the following pool issue prices (per metric ton) of fertilizers in respect of sales to (i) different States and Union territories and to (ii) private parties for supplies to the distributors of fertilizers for consumption in tea, coffee and rubber plantations in Kerala, Madras, Mysore, Assam & W. Bengal with effect from Feb. 1, 1966. (i) *For State Governments & Union Territories:* (a) Ammonium Sulphate—Rs. 366.00 and Rs. 355.00 in 50 and 100 kg bags respectively; (b) Ammonium Sulphate Nitrate—Rs. 455; (c) Urea—Rs. 610.00; (d) CAN—Rs. 315.00; and (e) Ammonium Phosphate (20-20-0)—Rs. 590.00; (ii) *For Private Parties:* (a) Ammonium Sulphate—Rs. 396.00 and Rs. 385.00 in 50 and 100 kg. bags respectively; (b) Double Salt—Rs. 492.00; (c) Urea—Rs. 650.00; and (d) CAN—Rs. 344.00.

[Circular Letter of the Union Ministry of Food & Agriculture, Jan. 29, 1966]

Rain Making with Urea

Trials by the universities of Chicago and Wisconsin with the support of the National Science Foundation, U.S.A. have shown that cloud dusting with urea is a distinctly possible method of inducing rainfall. The trials were carried out by aircraft this summer over northern Wisconsin. Urea is stated to have been found as effective for the purpose as silver iodide or dry ice over which it has the advantage of lower cost.

[NPKS Abstracts, Vol. 47, Nov. 1965]

Polyphosphate Fertilizers

New fertilizers, now being studied by Tennessee Valley Authority, Wilson Dam, Ala., are ammonium polyphosphate, calcium polyphosphate containing 56 per cent P_2O_5 and potassium polyphosphate containing 55 per cent P_2O_5 and 35 per cent K_2O. The latter is made by reacting potassium chloride with phosphoric acid at 600-1600°F.

Ammonium polyphosphate (16-16-0) is produced from superphosphoric acid and ammonia. The product is entirely water-soluble and contains about half its phosphate in the non-ortho form. It can be used for direct application, in bulk blends, or in making liquid fertilizers either alone or by the addition of potash, ammonia, another supplemental nitrogen material. Tests have indicated that ammonium polyphosphate is one of the better carriers of micronutrients and can also be used as a sequestrant in the production of liquid fertilizer from wet-process phosphoric acid. Other advantages are that it can be stored in bulk at a lower cost than the acid or base solution and can be transported at a lower cost per ton of plant nutrients.

[NPKS Abstracts, Vol. 47, Nov. 1965]

World's Largest Single Train Phosphoric Acid Plant

The world's largest single train phosphoric acid plant, with more than 600 s. tons annual capacity of Olin Mathiesen Chemical Corp. at Pasadena (Texas), began production on 26th May 1965. Some new facilities, best known as air and water pollution control performance and new phosphate rock grinding method which doubles the output, have been incorporated to provide the highest degree of efficiency. Between 96 and 97 per cent of phosphoric acid from the phosphate rock will be recovered due to new tanks and slurry cooling system, and this is the highest degree of recovery known at present. 55 tons of phosphate rock is ground in a large steel drum and is sent to concrete storage bins and then reacted with sulphuric acid to produce high analysis ammonium phosphate.

[Phosphorus & Potassium, No. 19, Oct. 1965]

We regret to record the sad demise of Sri Shanti Swarup, Chief Mechanical Engineer of this Division, on February 18 as a result of injuries sustained in the Caravelle jet crash at Palam airport on February 15.

Sri Swarup took B.Sc. (Engg) degree from the Benaras Hindu University in 1944 in First Division. He was an Associate Member of the Institution of Electrical Engineers. Before joining Sindri, he worked with Messrs Aluminium Corpr. of India for five years as Power Station Engineer and later for several years in the Calcutta Electric Supply (1949-52).

Sri Swarup joined Sindri in 1952 as a Shift Engineer and rose to Chief Mechanical Engineer in 1963. He took over charge as C.M.E. in the Planning and Development Division in March 1965.

He leaves behind his wife, two children and a host of friends and well-wishers to mourn his loss.

STATISTICS

TABLE 1—Year-wise Break-up of Fertiliser Demand in the fourth Plan and Imports

(in million tonnes)

Year	*N*			*P_2O_5*			*K_2O*
	Minimum requirements	*Indigenous production*	*Import requirements*	*Minimum requirements*	*Indigenous production*	*Import requirements*	*Import requirements*
1966-67	1.00	0.400	0.600	0.370	0.238	0.132	0.20
1967-68	1.35	0.525	0.825	0.500	0.269	0.231	0.30
1968-69	1.70	1.100	0.600	0.650	0.506	0.144	0.45
1969-70	2.00	1.400	0.600	0.800	0.629	0.171	0.56
1970-71	2.40	1.700	0.700	1.000	0.737	0.263	0.70

[Economic Times, Bombay, 18-3-1966]

TABLE 2—Proposed Targets of Agricultural Production by 1965-66 and 1970-71

Commodity	*Unit*	*Targeted production in* 1965-66	*Targeted production in* 1970-71	*Percentage increase*
Foodgrains ..	Million tons	92.00*	120.00**	30
Potato ..	Million tons	3.50	5.00	43
Oilseeds ..	Million tons	7.50	10.00	33
Sugarcane (gur) ..	Million tons	11.00	13.50	23
Cotton ..	Million bales	6.30	8.50	35
Jute† ..	Million bales	6.20	8.00	29
Coconut ..	Million nuts	4,713	5,180	8
Arecanut ..	Thousand tons	102	110	8
Cashewnut ..	Thousand tons	136	320	141
Pepper ..	Thousand tons	30	35	16
Cardamom ..	Thousand tons	3.3	3.8	15
Lac ..	Thousand tons	50	60	20
Tobacco ..	Thousand tons	400	480	20
Tea ..	Thousand tons	377	454	26
Coffee ..	Thousand tons	75	85	13
Rubber ..	Thousand tons	50	80	60
Index Numbers				
Foodgrains ..		153.4	200.1	30
Non-foodgrains ..		172.2	214.0	24
All-Commodities ..		160.0	205.0	28

* Based on the estimate that by 1965-66, 14.00 million tons of wheat, 40.00 million tons of rice, 24.00 million tons of other cereals and 14.00 million tons of pulses will be produced.

** Based on the estimate that by 1970-71, 21.00 million tons of wheat, 51.50 million tons of rice, 29.00 million tons of other cereals and 18.50 million tons of pulses will be produced.

† Excludes mesta which may provide 2.00 million bales in the Fourth Plan. *Source*: Government of India, Planning Commission.

[Fertilizer Statistics 1964-65 (Fertilizer Assocation of India, New Delhi) 1965, p 289]

TABLE 3—STATEWISE DISTRIBUTION OF AMMONIUM PHOSPHATE SULPHATE (16-20-0) DURING THE CALENDAR YEAR 1965

(m. tonnes)

State		*January to March* 1965	*April to June* 1965	*July* 1965	*August* 1965	*September* 1965	*October* 1965	*November* 1965	*December* 1965	*Total January to December* 1965
Andhra Pradesh	..	2,535	878	383	239	357	216	239	627	5,474
Bihar	..	1	—	—	—	—	—	—	—	1
Gujarat	..	204	256	48	266	23	44	22	—	863
Kerala	..	1,376	1,574	472	327	338	918	457	371	5,833
Madhya Pradesh	..	—	—	—	—	—	—	—	1	1
Madras	..	5,119	7,599	5,220	3,722	2,839	2,227	1,956	2,949	31,631
Maharashtra	..	734	300	94	330	—	—	72	48	1,578
Mysore	..	1,148	1,726	1,031	970	791	385	179	276	6,506
Orissa	..	—	66	1	—	—	—	—	—	67
Uttar Pradesh	..	—	25	—	—	—	—	—	6	31
Delhi	..	—	6	—	—	—	—	—	—	6
West Bengal	..	—	—	—	—	—	—	8	—	3
Pondicherry	..	119	30	5	28	92	26	75	21	396
Goa	..	—	212	166	44	—	47	96	—	565
Others	..	—	—	—	—	32	—	—	—	32
TOTAL	..	11,236	12,672	7,420	5,926	4,472	3,863	3,105	4,293	52,987

[Fertilizer News, Vol. 2, No. 3, 1966]

TABLE 4—STATEWISE DISTRIBUTION OF SUPERPHOSPHATE (16% P_2O_5) DURING THE CALENDAR YEAR 1965

(m. tonnes)

State	January to March 1965	April to June 1965	July 1965	August 1965	September 1965	October 1965*	November 1965*	December 1965*	Total January to December 1965
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Andhra Pradesh	25,317	29,910	10,562	7,350	8,204	6,303	4,433	6,815	98,894
Assam	4,410	3,188	1,575	81	605	868	1,228	933	12,888
Bihar	7,687	2,504	2,101	1,995	2,064	1,842	2,416	1,765	22,374
Gujarat	32,332	36,620	5,536	5,994	6,504	8,599	7,267	1,604	104,456
Jammu & Kashmir	378	—	—	88	—	—	112	200	778
Kerala	2,725	6,572	1,524	880	1,124	1,880	1,810	1,218	17,733
Madhya Pradesh	22,227	18,176	2,119	4,106	1,284	1,688	7,267	7,418	64,285
Madras	13,221	11,932	7,203	4,177	5,231	5,185	2,320	4,824	54,093
Maharashtra	20,204	27,329	7,057	6,858	6,976	9,321	6,125	7,319	91,189
Mysore	15,525	15,539	3,146	4,041	4,305	1,442	1,579	1,484	47,061
Orissa	3,014	1,180	—	733	949	128	—	—	6,004
Punjab	6,960	5,780	3,212	3,404	1,440	1,870	2,016	2,321	27,003
Rajasthan	390	1,928	96	30	173	1,800	360	500	5,277
Uttar Pradesh	4,446	12,398	2,152	3,337	2,857	2,803	2,929	2,610	33,532
West Bengal	2,581	16,920	5,740	5,532	5,464	5,588	6,389	3,292	51,506
Delhi	55	68	151	112	102	90	125	51	754
Himachal Pradesh	1,269	1,591	264	220	66	—	—	94	3,504
Manipur	48	36	126	30	—	—	15	—	255
Tripura	—	—	—	—	—	—	46	—	46
Pondicherry	—	—	—	104	—	—	7	—	111
Andamans	—	51	—	—	—	—	—	—	51
Nagaland	31	30	—	—	—	—	—	—	61
TOTAL ..	162,820	191,752	52,564	49,072	47,348	49,407	46,444	42,448	641,855
Used in Mixtures Wastages & Stock	10,481	11,668	4,544	3,613	7,256	4,098	2.905	3,520	47,885
Adjustments	100	448	337	—	—	—	—	—	885
Free Supply	2	2	1	—	—	—	—	—	5
Nepal	64	—	—	—	—	—	—	115	179
GRAND TOTAL ..	173,467	203,670	57,446	52,685	54,604	53,505	49,349	46,083	690,809

* Provisional

[FAI Information Service, Vol. 7, No. 7, April 1, 1966]

TABLE 5—STATEWISE TARGETS OF CONSUMPTION OF FERTILIZERS* (1970-71)

(metric tonnes)

Sl. No.	State	Targets to be achieved by the end of the Fourth Plan		
		N	P_2O_5	K_2O
1.	Andhra Pradesh	2,32,478	1,29,146	79,457
2.	Assam	33,804	20,041	8,424
3.	Bihar	1,77,061	80,811	30,911
4.	Gujarat	1,12,314	52,254	2,631
5.	Kerala	65,619	46,014	49,864
6.	Jammu & Kashmir	10,423	4,088	2,197
7.	Madhya Pradesh	92,922	66,383	907
8.	Madras	1,47,578	1,00,552	54,063
9.	Maharashtra	2,38,484	91,542	24,446
10.	Mysore	1,20,553	75,222	23,856
11.	Orissa	79,855	35,344	6,672
12.	Punjab	1,65,593	52,770	26,632
13.	Rajasthan	1,06,485	32,867	5,934
14.	Uttar Pradesh	3,23,285	1,42,313	4,192
15.	West Bengal	86,852	49,008	7,350
16.	Delhi	1,569	523	431
17.	Himachal Pradesh	2,420	941	182
18.	Tripura	2,177	1,507	953
19.	Manipur	545	182	—
20.	Plantations	42,481	19,908	24,700
	TOTAL	20,42,498	10,01,416	3,53,802

Source: Ministry of Food and Agriculture, New Delhi.

Note: Statewise details corresponding to 2.40 million tons of N and 0.70 million tons of K_2O, as proposed by the Committee on Fertilizers; may be obtained by increasing the N figures by 20% while K_2O by 100%. Figure for P_2O_5 remains unaltered. These *pro-rata* increases give a fairly representative Statewise picture of Committee's targets to be achieved by 1970-71.

* Provisional.

[Fertilizer Statistics 1964-65 (Fertilizer Association of India, New Delhi) 1965]

TABLE 6—MANUFACTURE OF SULPHURIC AND NITRIC ACIDS IN INDIA

(Monthly Averages of Calendar Months)

Metric Tonnes

Year	*Sulphuric Acid*		*Nitric Acid*	
	Installed Capacity	*Production*	*Installed Capacity*	*Production*
1954	16,699	12,775	—	—
1955	17,606	14,072	—	—
1956	20,756	13,989	—	115
1957	23,123	16,601	—	116
1958	24,560	19,185	309	130
1959	31,673	24,738	,,	143
1960	39,622	29,495	698	452
1961	46,989	35,208	6,883	487
1962	58,519	39,122	,,	586
1963	68,410	47,346	45,251	690
1964	84,263	56,553	1,196	974
September	81,783	58,140	1,179	683
October	82,481	60,763	1,196	983
November	,,	53,805	,,	1,083
December	84,263	60,385	,,	1,272
1965				
January	84,597	59,535	1,149	1,380
February	,,	56,652	,,	1,162
March	87,399	59,118	,,	1,440
April	,,	52,159	,,	1,280
May	,,	59,362	,,	1,454
June	,,	57,594	,,	1,315
July	,,	58,462	,,	816
August	90,193	45,060	,,	1,075
September	,,	—	—	—

[Monthly Statistics of the Production of Selected industries of India, Vol. XVII, No. 9, Central Statistical Organization, 1965]

TABLE 7—PRODUCTION, IMPORTS AND DISTRIBUTION OF FERTILIZERS DURING 1952-53 TO 1964-65

(metric tonnes)

Year	Nitrogen[1] (N)			Phosphoric Acid[1,2] (P_2O_5)			Potash (K_2O)	
	Produced	Imported[3]	Distributed[4]	Produced	Imported	Distributed[5]	Imported	Distributed[6]
1952-53	53,067	44,294	57,822*	7,445	—	4,552	3,311	—
1953-54	52,905	19,346	89,287*	13,831	—	8,261	7,490	—
1954-55	68,478	19,984	94,810*	14,345	—	15,027	11,097	—
1955-56	76,859	53,379	107,494*	12,365	—	13,018	10,265	—
1956-57	78,788	56,768	123,054*	17,585	—	15,874	14,791	—
1957-58	81,144	110,100	149,019*	25,785	—	21,922	12,786	—
1958-59	80,766	97,540	171,988*	30,987	—	29,490	22,366	—
1959-60	83,694	142,335	229,320**	51,407	3,819	53,930	33,103	21,342
1960-61	111,987	171,926	211,685**	53,722	128	53,134	24,845	29,052
1961-62	154,326	142,920	291,536**	65,360	645	63,932	30,381	27,982
1962-63	194,194	229,462	360,033**	88,300	7,959	89,940	44,276	36,503
1963-64	219,072	197,691	(406,976)**	107,836	12,267	(116,674)	64,060	(50,570)
	—	—	425,895	—	—	121,047	—	51,860
1964-65	243,230	256,517	(434,473)**		—	(147,652)	—	(70,440)
	—	—	492,249**	130,464	12,293	147,269	57,176	71,640

* Allotments of fertilisers under the "Central Fertiliser Pool".

** Actual despatches of fertilisers under the "Central Fertiliser Pool".

Note: 1. Includes complex fertilisers which contain both N and P_2O_5.

2. Excludes bonemeal and ground rock phosphate for which data are not available.
3. Figures from 1952-53 to 1957-58 are on financial year (April-March) basis.
4. Figures from 1952-53 to 1956-57 relate to calendar years ending in the first half of the period stated while from 1957-58 to 1962-63 they are on financial year (April-March) basis. In respect of 1963-64 and 1964-65 figures are furnished both on financial year as well as agricultural year (July-June) basis, the former being in brackets.
5. Figures from 1952-53 to 1957-58 refer to calendar years ending in the first half of the period stated while from 1958-59 to 1962-63 they are on financial year (April-March) basis. In respect of 1963-64 and 1964-65 figures are furnished both for financial year and agricultural year (July-June), the former being in brackets.
6. In case of sulphate of potash, quantity imported is taken as distributed. Figures relate to financial year (April-March). In respect of 1963-64 and 1964-65 figures are furnished both for financial year and agricultural year, the former being in brackets.

[Fertilizer Statistics 1964-65]

TABLE 8—STATISTICS OF RURAL COMPOST PRODUCTION AND AREA GREEN MANURED DURING 1962-63 TO 1964-65

State/Union territory	Rural compost (lakh tons)			Green manuring (lakh acres)		
	1962-63	1963-64	1964-65*	1962-63	1963-64	1964-65*
Andhra Pradesh	146.93	161.50	200.00	36.20	39.80	42.40
Assam	3.17	2.11	5.00	0.73	2.32	3.00
Bihar	19.50	23.17	26.00	7.33	6.73	10.00
Gujarat	2.63	3.23	3.95	1.17	1.64	1.35
Jammu and Kashmir	1.05	1.20	1.50	0.013	0.044	0.067
Kerala	2.25	2.57	3.15	5.12	6.19	8.00
Madhya Pradesh	14.28	17.68	18.00	3.28	4.89	7.44
Maharashtra	6.00	9.24	9.50	0.46	1.12	1.30
Madras	32.85	38.91	45.45	48.60	52.07	56.94
Mysore	36.43	17.38	15.00	4.03	6.02	7.00
Orissa	35.09	35.77	45.00	20.87	18.32	40.00
Punjab	91.01	94.78	84.00	5.75	7.35	8.00
Rajasthan	13.01	16.51	15.70	2.28	1.09	4.80
Uttar Pradesh	441.37	458.29	550.00	20.04	24.97	30.00
West Bengal	12.04	19.70	25.00	2.33	2.42	2.65
Delhi	0.30	0.35	0.35	0.013	0.011	0.02
Himachal Pradesh..	2.56	4.64	4.92	0.08	0.113	0.15
Manipur	0.65	0.68	0.68	0.012	0.016	0.025
Tripura	1.36	2.10	2.55	0.028	0.022	0.015
Pondicherry	0.28	0.29	0.30	0.22	0.21	0.30
Goa, Daman and Diu	—	0.20	0.25	—	0.012	0.05
Nagaland	—	—	—	0.004	0.012	0.005
N.E.F.A.	—	—	—	0.003	0.006	0.007
Andaman and Nicobar	0.039	0.012	—	0.016	0.016	0.006
TOTAL ..	862.799**	910.312**	1,056.30**	159.579	175.392	223.525
	or say 86 m. tons	or say 91 m. tons	or say 106 m. tons	or say 16 m. acres	or say 18 m. acres	or say 22 m. acres

* Subject to revision.

** In addition to this, farm yard manure produced in the country is roughly estimated at 216.00 million tons annually.

Source: Ministry of Food and Agriculture, Government of India.

[Fertilizer Statistics 1964-65, (Fertilizer Assn. of India, New Delhi) 1965]

TABLE 9—STATISTICS ON URBAN COMPOST PRODUCTION AND DISTRIBUTION

State/Union territory	Number of working centres		Compost produced (tons)		Compost distributed (tons)	
	1962-63	1963-64	1962-63	1963-64	1962-63	1963-64
Andhra Pradesh	324	322	230,748	164,251	184,598	129,124
Assam	14	14*	7,000	5,000*	5,600	2,000*
Bihar	53	54	90,804	90,881	80,980	80,208
Gujarat	121	171	95,605	87,841	81,468	80,557
Jammu & Kashmir	2	2*	8,000	3,000*	6,400	3,000*
Kerala	20	23	19,409	21,069	14,716	14,307
Madhya Pradesh	151	154	153,083	149,977	130,614	136,858
Madras	368	378	507,756	476,328	243,380	372,504
Maharashtra	229	265	280,257	321,544	231,783	381,617
Mysore	242	242*	352,600	375,000*	301,394	300,000*
Orissa	53	53*	21,500	16,000*	15,071	12,800*
Punjab	130	131	246,614	247,766	236,755	226,751
Rajasthan	97	120	276,000	296,000	220,800	177,600*
Uttar Pradesh	402	412	591,597	610,610	609,988	619,469
West Bengal	35	35	41,439	40,454	39,992	38,712
Delhi	1	1	28,179	26,128	28,179	26,128
Himachal Pradesh	7	5	490	509	489	295
Pondicherry	4	2	1,510	2,326	419	2,710
Tripura	1	1	1,310	1,749	1,023	557
Manipur	2	—	320	—	96	—
Cantonments	41	46	100,000	91,651	90,000	79,000
Miscellaneous	—	—	200,000	250,000	200,000	250,000
TOTAL	2,297	2,431	3,254,221	3,277,484	2,723,645	2,934,797

* Anticipated.
Source: Ministry of Food and Agriculture, Government of India.

[Fertilizer Statistics, 1964-65, (Fertilizer Assn. of India, New Delhi), 1966]

TABLE 10—PRODUCTION AT SINDRI FERTILIZERS FACTORY DURING 1960 TO 1965

Sl. No.	Year	Raw Materials Used, tonnes			Production, tonnes		
		Coking Coal	Gypsum	Steam Coal	Ammonium Sulphate	Double Salt Ammonium Sulphate Nitrate	Urea
1.	1960	290,277	534,830	376,479	295,576	35,428	8,668
2.	1961	310,539	555,761	375,389	284,320	52,343	13,192
3.	1962	316,340	671,873	406,516	321,465	57,767	17,048
4.	1963	325,351	669,794	447,966	315,622	49,923	18,713
5.	1964	302,709	611,582	422,176	300,470	46,626	17,411
6.	1965	312,811	674,409	420,560	333,995	52,074	20,019

[Production and Accident Statistics—A Look Back, Fertilizer Corporation of India Ltd., Sindri Unit, Feb. 1966]

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CONTENTS

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EDITOR'S NOTE

It has now been decided to publish in TECHNOLOGY research papers from scientists and technologists outside FCI Ltd., provided these are:

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Studies on CO-Conversion Catalyst

By

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The use of a Fe_2O_3-Cr_2O_3 type catalyst in the water gas shift reaction is well-known. In general, pressure operation of commercial units are associated with the problem of crumbling of the catalyst and formation of methane. The latter may be accounted for use of lower concentration of steam in pressure units tending to cause reduction to take place beyond Fe_3O_4 state, whereas, the phenomenon of crumbling is associated with some structural changes. The present investigation shows that during reduction of Fe_2O_3 to Fe_3O_4 the grain size increases and surface area decreases. Such change in size is likely to exert intergranular pressure tending to crumble the shape of the catalyst. It could be established that by changing the sequence of Cr_2O_3 addition, altering its concentration and by adjusting the time and temperature of heat treatment the fall in surface area and enlargement of grain size during reduction could be arrested. The results obtained with varying concentration of Cr_2O_3 in the range 0-20 per cent indicate that the effect on structural properties is not proportional to the increasing concentration of Cr_2O_3. The optimum concentration of Cr_2O_3 appears to be somewhere around 14 per cent.

The catalyst usually employed for the water gas shift reaction is of Fe_2O_3-Cr_2O_3 type. It is the iron oxide in the form of Fe_3O_4 which catalyses the reaction $CO+H_2O=CO_2+H_2$. In a conventional converter working at or nearabout atmospheric pressure, the general custom is to use excess steam, as high as 4 to 5 times the carbon monoxide concentration in the gas. The modern trend is, however, towards the operation of the converter at higher pressure, in the region of 12-30 atm., and therefore from economic point of view it is not desirable to run the pressure units with large excess of steam which is likely to reduce the throughput of the units. The normal practice is to run the units with steam corresponding to 2.5 to 3 times the concentration of carbon monoxide in the feed.

Increase of steam concentration in the feed increases the oxidation potential.[1] On the other hand, decreasing concentration of steam tends to decrease the oxidation potential and at the limiting stage causes Fe_3O_4 to get reduced to FeO and ultimately to Fe. This extreme condition is associated with crumbling of the catalyst and initiation of the methanation reaction. As a matter of fact, crumbling of catalyst during use is even today a problem to many industries employing shift reaction. In general, change in the sequence of Cr_2O_3 addition, altering its concentration, and adjustment of time and temperature of heat treatment contribute towards life and stability of this catalyst.

Considering all these aspects, the present investigation on a few batches of CO-conversion catalyst, before and after reduction, was carried out to examine the effect of increase of Cr_2O_3 concentration and heat treatment on surface area, pore size etc. and conversion efficiency in bringing about the structural changes in the catalyst. It was to examine how such changes can explain the stability and life of the shift catalyst.

Experimental

The investigations were carried out on six varieties of catalyst samples prepared at the catalyst plant of this Division. A brief outline of the methods of preparation of the samples are given below.

Sample 1: Iron oxide obtained from ferrous carbonate formed by reacting ferrous salt with ammonium carbonate. The iron oxide granules were dried at 120°C for 8 hours.

Sample 2: Same as sample 1, but heated above 350°C.

Sample 3: Same as sample 1, but mixed with chromium salts to give 7 per cent Cr_2O_3 in the finished catalyst.

Sample 4: Same as sample 3, but heated above 350°C.

Sample 5: Same as 4, but with 14 per cent Cr_2O_3.

Sample 6: Same as 5, but with 20 per cent Cr_2O_3.

The specific surface areas, and water, helium and mercury displacement volumes were determined to calculate the average grain and pore sizes of the reduced and unreduced samples. The surface area measurements were carried out by the B.E.T. method.

E. O. Wigg and A. J. Juhola[2] described a method for the measurement of pore volume by finding out the difference of water and mercury displacement volumes for investigation on catalyst. It is often desirable to obtain densities with both helium and mercury as the displacing fluid. The difference between these two can be used to calculate the pore volume as described by R. B. Anderson et al.[3]

In the present case the apparatus used for the determination of helium densities was the same as described by R. J. Kokes[4] except that for mercury density determinations slight modification was made. The average grain radius and the average pore radius were calculated from the following equations:

$$(a)\ \bar{r}g = \frac{3}{S \times D}$$

$$(b)\ rp = \frac{2V}{S}$$

where, rg = average grain size
rp = average pore radius
V = total pore volume
S = surface area
D = apparent density of particles

The activity tests of all the samples were carried out under the same operating conditions in an equipment similar to that described earlier[5].

The semi-water gas obtained from the production plant of Sindri Unit had the following percentage composition: CO_2 8.6; CO 33.8; O_2 nil; H_2 35.6; CH_4 0.6; and N_2 difference, and was used for the determination of conversion efficiency.

Results & Discussion

The variations of surface areas and pore volumes in all the catalysts, before and after reduction, have been determined to find out the effect of chromium incorporation, and the optimum chromium concentration level. The results are shown in Tables 1-3. It may be mentioned here that the total pore volume that can be obtained with water and mercury displacement methods cover the ranges of pores lying between 10Å to 10μ respectively.

It can be seen from Tables 2 and 3 that in each case the helium and mercury displacement values descrease after reduction. The decrease in true volume is not proportionate to the apparent volume, thus resulting in the decrease of total pore volume after reduction.

From the above tables, it is also evident that the average particle size increases after the reduction with decrease of surface area. This phenomenon is accompanied with the change of Fe_2O_3 to Fe_3O_4.

One important point may be noted while drawing a comparison of average pore and grain size of reduced and unreduced catalysts that the reduction process is accompanied by coalescing of grains and small pores to large ones as is evident from the results (Tables 2 & 3). The increase in pore size after reduction is nearly one and half times its original value in each case except for sample 1 (without chromium) where the increase is more than two-fold. The unusual increase in pore diameter in sample 1 is attributed to the different changes which take place in the structure of Fe_2O_3 during reduction. The observation also points out to the fact that these changes are not so pronounced in other samples, which may be due to incorporation of chromium which probably provides support to the skeleton structure of iron oxide.

The process of the change of the surface properties on heating of iron hydroxide gel prepared by the precipitation methods has been studied[6]. The gel is composed of small grains and starts crystallising evolving heat in the process of heat treatment and decrease in surface area takes place.

It is known from X-ray investigation[7] that upto a temperature of 500°C the following changes take place in the crystal shape, as

$$\underset{\text{(rhombic)}}{FeO.OH} \xrightarrow{250^\circ C} \underset{\text{(cubic)}}{Fe_2O_3} \xrightarrow{400^\circ C} \underset{\text{(hexagonal).}}{Fe_2O_3}$$

In spite of the change of the size of the primary crystal, the grains remain needle-shaped and their sizes also do not change, and only when it is heated to 750°C the needle-shaped crystals change into lumpy grains. In view of these, it appeared that D.T.A. curve at this temperature range could provide some information regarding structural changes of finished catalyst.

In Fig. 1, the curves of samples 1 and 2 are shown, The first endothermic peak at about 100°C represents the evolution of moisture in both the samples, while, the second endothermic peak in sample 1 from 270°C to 300°C represents the change of FeO.OH (rhombic) to γ-Fe_2O_3 (cubic form). This peak is practi-

TABLE 1

Sample No.	Form	Size, mm.	Cr_2O_3, %	Loss on Ignition at 900°C for 2 hr, %	Crushing Strength, kg./cm²		Conversion, %	
					Before use	After, 100 hr. use	Initial	Final
1.	Pellet	10×10	Nil	14.5	80	Crumbles to Powder	84.5	—*
2.	-do-	-do-	Nil	3.0	89	Low	84.2	72.0
3.	-do-	-do-	7.0	15.9	110	39	89.0	88.0
4.	-do-	-do-	7.0	2.9	227	361	86.5	84.0
5.	-do-	-do-	14.0	2.9	235	366	87.0	86.0
6.	-do-	-do-	20.0	2.75	231	360	87.0	86.5

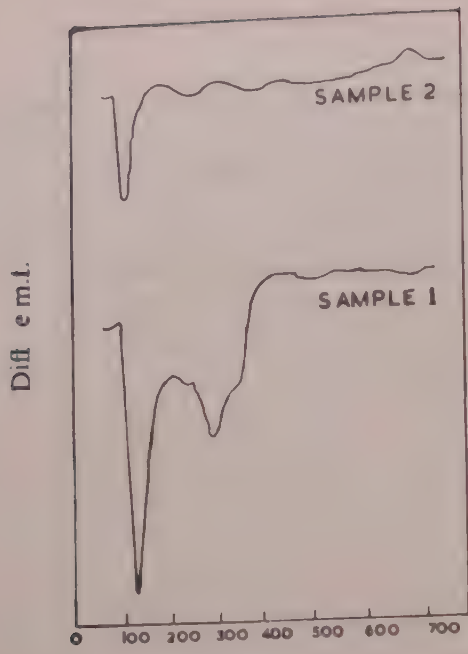
*Experiment could not be carried out due to carrying-over of catalyst powder and subsequent choking of the reactor tube.

TABLE 2—STUDY OF CO-CONVERSION CATALYST
(Before Reduction)

Sample No.	Vol. from Water Displacement, c.c./g.	Vol. from Hg Displacement, c.c./g.	Vol. from He Displacement, c.c./g.	Total Pore Volume=V, c.c./g.	Specific Gravity, g./c.c.	Surface Area, m²/g.	$\bar{r}$ of Grain, Å	$\bar{r}$ of Pores, Å
1.	0.243	0.791	0.239	0.55	4.18	35.38	671	310
2.	0.180	0.53	0.180	0.35	5.55	23.55	675	297
3.	0.251	0.62	0.244	0.37	4.09	39.29	473	188
4.	0.210	0.48	0.203	0.28	4.92	30.3	475	184
5.	0.207	0.462	0.201	0.26	4.97	28.0	494	185
6.	0.195	0.44	0.186	0.24	5.38	26.81	492	179

TABLE 3—STUDY OF CO-CONVERSION CATALYST
(After Reduction)

Sample No.	Vol. from Water Displacement, c.c./g.	Vol. from Hg Displacement, c.c./g.	Vol. from He Displacement, c.c./g.	Total Pore Vol. =V, c.c./g.	Specific Gravity g./c.c.	Surface Area, m²/g	$\bar{r}$ of Grains, Å	$\bar{r}$ of Pores Å
1.	0.208	0.644	0.204	0.44	4.89	12.57	1537	700
2.	0.170	0.454	0.167	0.287	5.98	11.80	1154	486
3.	0.218	0.565	0.209	0.356	4.78	19.35	876	368
4.	0.202	0.448	0.196	0.252	5.10	18.36	732	274
5.	0.181	0.420	0.174	0.247	5.76	17.82	707	277
6.	0.184	0.405	0.180	0.225	5.55	17.97	676	250

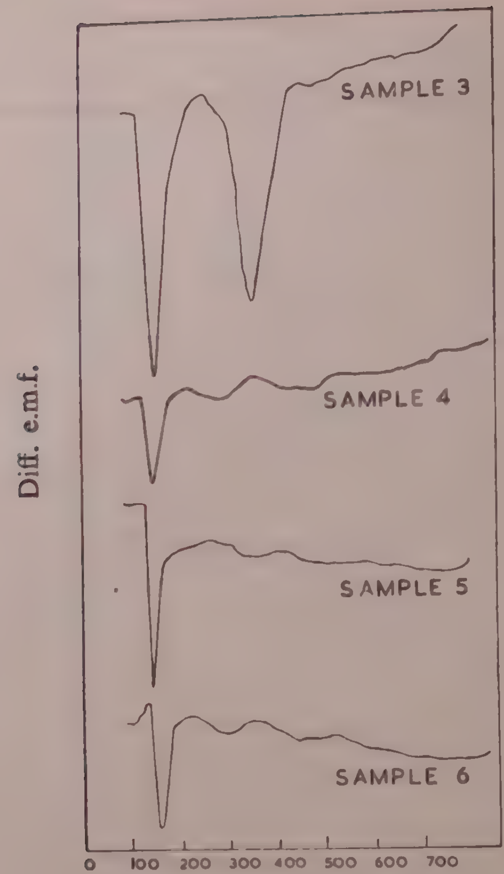


Temp. °C
Fig. 1

cally absent in sample No. 2, as the sample was pretreated at a higher temperature. The exothermic change of γ-Fe_2O_3 (cubic) to Fe_2O_3 (hexagonal) is not marked in these curves, presumably due to the continuous evolution of water associated in the crystal lattice, which is more pronounced in these samples and may be attributed to the method of preparation. Nevertheless, slight tendency of the curves to pop up at about 450°C indicating presence of exothermic peak can be observed.

Fig. 2 represents DTA curves of another set of CO-conversion catalyst samples (Nos. 3, 4, 5 and 6). The initial evolution of moisture is represented by a small endothermic peak at 140-150°C, in all the cases. Again, the curves are essentially identical except for sample 3, which shows a well-marked endothermic peak at 300°C representing the change from FeO.OH to Fe_2O_3. In other samples, a small depression (endothermic) at 250-290°C indicates the change of FeO.OH to γ-Fe_2O_3. A small hump at 490-540°C represents the change from γ-Fe_2O_3 (cubic) to Fe_2O_3 (hexagonal), which is also not very prominent in these samples due to the same reason as described earlier. The addition of chromium upto 20 per cent does not indicate any particular change in the nature of the curve as is evident from the DTA curves upto the temperature ranges studied.

Since Fe_3O_4 and not Fe_2O_3 is the active form to act as a catalyst for the CO-conversion, the so-called active centres are produced in the midway of the change taking place from Fe_2O_3 to Fe_3O_4. It has already been observed that greater the decrease in surface area, the more facile is the conversion of smaller pores of Fe_2O_3 to bigger ones.



Temp °C
Fig. 2

The results indicate (Table 1) that activity of the sample 1 drops within a short interval of time and the catalyst tablets crumble to powder during the progress of reaction. This sample, having 14.5 per cent water which is not released below 270°C, has the structural water corresponding to the configuration, FeO.OH. Further, it is observed that when this sample is reduced, the extent of increase of grains size is more than any of the samples studied. The fall of activity may be accounted due to the shrinkage of surface leading to lowering of surface area. The fall in crushing strength leading to crumbling of well formed hard tablets is due to the combined effect of release of structural water at the reaction temperature and large growth of grains which is likely to develop due to intergranular pressure.

Comparing the results of samples 1 and 2, it is found that in case of the latter, which is actually a cured form of sample 1, the conversion efficiency drops but there is slight improvement in stability of the catalyst pellets. It is also observed that the drop in activity is associated with lowering in surface area. The extent of enlargement of grain size due to reduction is much less in case of the sample 2. This and the fact that more than 98 per cent of the structural water is removed during heat treatment accounts for improvement in stability of the catalyst tablets.

When Cr_2O_3 is incorporated in sample 1, the surface area is increased (sample 3) and the average radius of the grains is reduced. This catalyst shows distinct improvement both in percentage conversion and stability over sample 1. Its surface area when reduced, does not decrease to the same extent as in the case of sample 1. Moreover, the enlargement of grain size due to reduction is much less. Thus, the presence of Cr_2O_3 from structural point of view functions in two ways, viz. (a) to prevent the tendency of shrinkage of the surface during reduction and, (b) it reduces the extent of enlargement of grain size during appearance of Fe_3O_4.

Conclusion

Heat treatment adopted for the preparation of CO-conversion catalyst causes decrease in surface area but can stabilize the activity and crushing strength of the catalyst. Presence of chromium reduces the extent of lowering of surface area on reduction is clear from the results obtained with samples 1 and 3 (Table 2). In cured samples also the same effect of chromium can be noticed. Both, addition of Cr_2O_3 and curing at a high temperature can improve stability of the shift catalyst. The reduction operation of iron oxide conversion catalyst is always associated with the lowering of surface area. Chromium when present in the catalyst substantially arrests the fall in surface area during reduction. This structural effect of chromium is, however, not proportional to its increasing concentration. The optimum Cr_2O_3 concentration appears to be somewhere around 14 per cent.

The overall effect of Cr_2O_3 on increase of activity and stability are respectively due to increase in surface area of the reduced sample and lowering of inter-granular pressure due to increase in size of grains during reduction.

For making a catalyst suitable for industrial use, it is essential to impart stability along with conversion efficiency. In preventing crumbling of catalyst during use, it is necessary to check the tendency of the grains to grow during reduction. Moreover, the grains should not show high loss of surface area on reduction. Both the requirements as far as the results of the present investigations are concerned can be fulfilled by suitable curing and chromium addition.

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Corrosion of Mild Steel by Hydrogen Sulphide in an Ammoniacal Medium

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Corrosion of mild steel by H_2S has been studied in an ammoniacal medium at 35 and 50°C. A maximum corrosion rate has been observed at H_2S concentration of 1.5 g./l. Potential measurements after 6 hours indicate that most negative potential was reached at H_2S concentration of 0.5 g./l. An increase in temperature from 35 to 50°C increased the corrosion rate, which is also accelerated by sodium chloride.

Mild steel equipment are used extensively for handling ammoniacal solutions and are considered resistant to them but failures occur under certain conditions[1]. Recently some mild steel equipment had failed in an ammoniacal medium in the fertilizer factory at Rourkela[2]. The failure occurred in the spent liquor regeneration section of the plant in the temperature range 30 to 60°C. The trouble was traced due to the presence of hydrogen sulphide in the liquor which caused stress-corrosion failure of mild steel[3,4]. Corrosion of mild steel by hydrogen sulphide has been reported widely in literature[4–19], and several workers have made detailed investigations into the mechanism and other aspects of such corrosion. In all the cases so far studied, the corroding agent has been hydrogen sulphide in presence or absence of carbon dioxide, water, brine and oxygen but no study seems to have been carried out on corrosion of mild steel by hydrogen sulphide in an ammoniacal medium. In fact, ammonia has been used by some workers[19,20] to inhibit the corrosion by hydrogen sulphide.

Studies were, therefore, undertaken on the corrosion of mild steel in dilute ammonia solution containing different concentrations of hydrogen sulphide. Weight-loss as well as electrode potential measurements were carried out, the results of which are reported in this paper.

Experimental

In all the experiments performed in an ammoniacal medium, a 2N solution of ammonia was used, while double-distilled water was used in those performed in absence of ammonia. Solutions having different concentrations of hydrogen sulphide were obtained by passing the gas for intervals of time through the liquor which was finally analysed[21]. Sodium chloride and ammonia solutions used were of BDH (A.R.) grade.

For all the weight-loss as well as potential measurements, rectangular test coupons of $6.2 \times 1.5 \times 0.5$ cm size were cut out from M. S. Sheet*. A 6 mm. diam. hole was drilled in each of them. For surface preparation and degreasing, the previous procedure[22] was adopted. In each case, exact measurements of the coupons were made by callipers. The coupons were kept completely immersed in the respective solutions (450 ml.) taken in a 500 ml. Erlenmeyer flask, to the lower portion of which a glass tube with a porous sintered glass fused inside it was sealed. The other and of the tube was sealed to a vertical tube of the same diameter. The side arm and the connecting tube were filled with the same solution as in the flask. The solution in the flask was tightly stoppered and kept in an water-bath maintained at 35 ± 0.1 and 50 ± 0.1°C respectively. The coupons were hung by glass hooks inserted through holes in the rubber stoppers of the flasks.

For weight-loss measurements, the coupons were kept immersed for 6 hours and at the end of the period, after removing the adhering corrosion product, they were treated with the inhibited acid[23], dried and weighed;

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*Specification I.R.S.M. 16/49, manufactured by Tata Iron & Steel Co. Ltd.

TABLE 1—CORROSION OF MILD STEEL IN DILUTE AMMONIACAL LIQUOR BY HYDROGEN SULPHIDE

Expt. No.	NH_3 Concentration, g./l.	H_2S Concentration, g./l.	Temperature 35°C			Temperature 50°C			Remarks
			Potential after 5 Min. Vs S.C.E., mv	Potential after 6 Hr. Vs. S.C.E. mv	Corrosion Rate, mg./sq. dm./day	Potential after 5 Min. Vs. S.C.E., mv	Potential after 6 Hr. Vs. S.C.E. mv	Corrosion Rate, mg./sq. dm./day	
1.	34	—	−186	− 103	No corrosion	−186	− 103	No corrosion	Corrosion product was thin, uniform and adherent and could not be removed by rubbing.
2	34	0.05	−221	− 158	-do-	−292	− 345	-do-	
3	34	0.10	−366	− 983	8.8	−521	− 961	15.7	
4	34	0.2	−418	− 997	16.0	−542	− 990	28.3	
5	34	0.5	−492	−1016	20.0	−560	−1003	31.4	Corrosion product was thick and non-adherent.
6	34	1.0	−525	−1009	23.5	−975	− 955	46.4	
7	34	1.5	−548	− 986	43.8	−988	− 902	53.5	
8	34	2.5	−560	− 903	38.2	−990	− 882	42.7	Corrosion product was thin, uniform and partly adherent; some portion of the deposit could be removed by rubbing.
9	34	5.0	−583	− 790	32.4	−993	− 664	34.6	
10	34	7.5	−658	− 718	27.4	−995	− 624	28.7	
11	34	10.0	−965	− 680	25.5	−997	− 622	26.1	
12	34	12.5	−883	− 631	19.4	−969	− 618	21.2	
13	34	15.0	−863	− 630	17.5	−904	− 617	18.4	Corrosion product was thin, uniform and adherent.
14	34	20.0	−622	− 634	12.5	−828	− 611	14.0	
15	34	25.0	−618	− 631	7.5	−810	− 612	7.7	
16	34	30.0	−608	− 633	5.5	−800	− 611	5.6	

the loss in weight was recorded as mg./sq. dm/day. For potential measurements a wire of the same composition as that of the electrode was fixed to the latter and was taken through the stopper and finally connected to the potentiometer. The liquor in the side arm was in contact with the same solution kept in a small beaker which was ultimately connected through the saturated calomel electrode to the potentiometer. All potential measurements were done with a potentiometer† using an external galvanometer. The potential values were recorded from 5 min. after the start of the experiment upto 6 hours when a steady state had been reached. The values in Table 1 are the starting ones taken after 5 min. and the steady state ones are recorded at the end of 6 hours.

Results & Discussion

Weight-loss Experiments in Absence of Chloride: The results (Table 1) clearly show that mild steel is not corroded in 2N ammonia at 35°C, and even upto a dissolved hydrogen sulphide concentration of 0.05 g./l. there was no corrosion. With a further increase in the concentration, the corrosion rate increased and reached its maximum value, viz. 43.8 mdd, at hydrogen sulphide content of 1.5 g./l. after which it decreased with the increasing amounts of hydrogen sulphide finally reaching a value of 5.5 mdd at hydrogen sulphide concentration of 30 g./l. The latter corrosion rate is even less than that at hydrogen sulphide concentration of 0.1 g./l. Similar behaviour was observed at 50°C also; there was no corrosion in pure ammonia upto a hydrogen sulphide concentration of 0.05 g./l. but afterwards the weight-loss increased with increase in the concentration reaching a maximum of 53.5 mdd at hydrogen sulphide concentrations of 1.5 g./l.; with further increase in the concentration, the corrosion rate decreased, viz at a hydrogen sulphide content of 30 g./l. the rate was only 5.6 mdd, which is about one-third of that observed at hydrogen sulphide content of 0.1 g./l.

Similar behaviour has been observed by other workers[6,12,16,18] in solutions of hydrogen sulphide containing no ammonia, and a maximum corrosion rate had been observed at a particular concentration of hydrogen sulphide, the corrosion decreasing in solutions containing higher or lower proportion of hydrogen sulphide. They also observed a minimum corrosion rate at a very low concentration of hydrogen sulphide, which was not observed in the present experiments.

†Manufactured by Pye Ltd. Cambridge, U.K., Cat No. 7569/P.

An examination of the test coupons showed a correlation between the corrosion rate and the nature of corrosion products. At low rates whether at low (0.1-0.2 g./l.) or high (15.0-30 g./l.) concentrations of hydrogen sulphide, the corrosion products were thin and adherent and could not be removed by rubbing with rubber stopper, etc., whereas at high corrosion rates (H_2S concentration 0.5 to 1.5 g./l.), they were thick, totally non-adherent and easily removable by rubbing. The nature of the corrosion products in the hydrogen sulphide concentration range 2.5 to 12.5 g./l. was thin and partly adherent, and the corrosion rate was less. For hydrogen sulphide concentrations 0.1 to 1.5 g./l., the corrosion rate increased approximately 1.5 to 2 times with temperature from 35 to 50°C, while at high concentrations the rates were nearly the same at both the temperatures. Because of the adherent nature of the product in the hydrogen sulphide concentration range 2.5 to 30 g./l. increase in temperature had little effect on the corrosion rate; whereas because of the non-adherent nature of corrosion product in the range of concentration of 0.5 to 1.5 g H_2S/l the corrosion rate increased markedly with increased temperature. It can, thus, be concluded that hard, adherent coating prevents further diffusion of reactants to the metallic surface and it is mostly formed at higher concentrations of hydrogen sulphide. Shannon and Boggs[10] have also observed that high concentration of hydrogen sulphide favours the formation of a hard coating which prevents further diffusion to the metal surface, while lower concentration favours the formation of non-adherent deposit which is easily removable. Greco and Wright[12] also made similar observations.

Investigations by previous workers have shown that the rate of corrosion of mild steel in aqueous solutions of hydrogen sulphide depend upon the nature of the sulphide film formed on the steel; the following types of film have been detected in presence of aqueous hydrogen sulphide[9,18]: kansite Fe_9S_8; trollite FeS; pyrrhotite $Fe_{0.875}S$; marcasite $FeS_{1.965}$; and pyrite FeS_2.

Studies by Meyer et al[9] have shown that the formation of a thicker kansite scale from kansite tarnish accelerates the corrosion rate but as the scale is superimposed with multiple scale growth of pyrrhotite and pyrite the rate decreases. Sardisco et al[16] have observed that at low corrosion rates the film consisted of marcasite or pyrite, trollite and some kansite, while at a high rate it consisted of trollite, pyrite and a predominating amount of kansite. Riggs and Radd[24] also concluded that kansite is an accelerator of corrosion while pyrite is a retarder.

The variation of corrosion rate with increasing concentration of hydrogen sulphide in the present study may also be explained as due to the initial building up of kansite scale from kansite tarnish and then the transformation of this scale partly or wholly into more protective sulphide films, like trollite, pyrhotite, marcasite and pyrite, with the falling off in the corrosion rate.

Effect of Sodium Chloride in Hydrogen Sulphide Solutions on Corrosion Rates: It will be observed (Table 2) that there is a slight tendency towards corrosion in aqueous ammonia (34 g./l.) solutions containing sodium chloride, even in the absence of hydrogen sulphide. In the range hydrogen sulphide 0.1 to 2.5 g./l. the corrosion rate is high in absence of ammonia when chloride is present; it first increases with the increase in chloride concentration but tends to decrease as the sodium chloride content is increased to 5000 ppm. Within the same range of hydrogen sulphide concentration in presence of ammonia, the corrosion rate is slightly higher in presence of a chloride than in its absence but again it tends to decrease as the sodium chloride content is increased to 5000 ppm. Such a decrease in the corrosion rate at a higher sodium chloride concentration was observed by Shannon and Boggs[10] in their corrosion studies on aqueous hydrogen sulphide systems in absence of ammonia. They postulated that at higher concentrations, chloride might be acting as an inhibitor by being absorbed on the metal surface.

The increased corrosion rate in presence of chloride may be ascribed to the promotion of a non-portective scale.

Potential Measurements: Electrode potential data generally give a good indication of corrosion of a metal in solutions, although, because of the various factors which determine the potential of an electrode in solution, there may not be an exact parallelism between the electrode potential and the rate of corrosion. Ewing[7] determined the potential of mild steel in solutions of hydrogen sulphide at different pH values (adjusted by adding caustic soda, wherever necessary) and found the values to lie between —705 to —800 mv (Vs. Sat. Cal. Electrode) in the pH range 4.3 to 8.4. Ulanovskii et al[25] also determined the potential of steel in aqueous solutions of hydrogen sulphide of different pH values and found a maximum negative potential of —829 mv (Vs Sat Cal. electrode). These workers have attributed the change in electrode potential to changes in pH of the solution and have not taken into account any possible role of the nature of the sulphide film formed on steel. The electrode potential measurements of mild steel in the present study (Table 1) were carried out in aqueous solutions of ammonia containing different concentra-

TABLE 2—EFFECT OF VARYING CONCENTRATION OF CHLORIDE IN PRESENCE AND ABSENCE OF HYDROGEN SULPHIDE AND AMMONIA AT 50°C.

Expt. No.	H_2S Concentration, g./l	NH_3 Concentration, g./l	NaCl Concentration, ppm	Corrosion Rate, mg./sq. dm./day	Remarks
1	—	34	50	2.0	Test coupon bright and shining.
2	—	34	200	2.0	
3	—	34	1000	2.3	
4	2.5	—	1000	385.6	Corrosion product thick, non-adherent and blistering occurred.
5	2.5	—	2000	425.6	
6	2.5	—	5000	359.8	
7	1.5	34	1000	59.3	Corrosion product thick and non-adherent.
8	1.5	34	2000	67.2	
9	1.5	34	5000	55.6	
10	1.5	—	—	326.2	Corrosion product thick and non-adherent and severe blistering occurred.
11	1.5	—	1000	401.2	
12	1.5	—	2000	438.1	
13	1.5	—	5000	394.9	
14	0.5	34	1000	41.6	Corrosion product thick and non-adherent.
15	0.5	34	2000	53.6	
16	0.5	34	5000	36.7	
17	0.5	—	—	186.2	Corrosion product was thick and non-adherent and severe blistering occurred.
18	0.5	—	1000	377.2	
19	0.5	—	2000	402.1	
20	0.5	—	5000	315.3	
21	0.1	34	1000	29.7	Corrosion product thin and non-adherent.
22	0.1	34	2000	33.7	
23	0.1	34	5000	28.1	
24	0.1	—	1000	243.1	Corrosion product thick-non-adherent and some blisters observed.
25	0.1	—	2000	277.1	
26	0.1	—	5000	130.6	

tion of hydrogen sulphide and the pH values were in the range 10.5 to 11.0. Previous workers did not measure the electrode potentials in hydrogen sulphide solution in this pH range.

The results (Table 1) show that there is no corrosion of mild steel in pure ammonia solution; the starting potential after 5 min. is −186 mV and the stable potential at the end of 6 hours is −103 mV both at 35 and 50°C. At 35°C with an increase in hydrogen sulphide concentration the starting potential becomes more negative and attains a maximum negative value of −965 mV at a hydrogen sulphide concentration of 10 g./l.; it then goes on decreasing with further increase in hydrogen sulphide concentration. The stable potential after 6 hours also follows a similar pattern and with increase in hydrogen sulphide concentration the potential becomes more and more negative and attains the maximum negative value of −1016 mV at a hydrogen sulphide concentration of 0.5 g./l. and then decreases with a further increase in hydrogen sulphide concentration. The general trend at a particular hydrogen sulphide concentration is that starting from a less negative value the potential values become more and more negative with time and the most negative potential value is attained in about 15 to 45 min. period; afterwards the potential values gradually fall and attain a stable value in about 6 hours. The potential measurements at 50°C also follow a similar pattern except that for a particular hydrogen sulphide concentration the starting potential is more negative than at 35°C while the stable potential is slightly less negative than at 35°C. The general trend at a particular hydrogen sulphide concentration is that starting from a less negative value the potential attains its most negative value in about 15 min. and thereafter registers a gradual fall and attains a stable value within 6 hours from 0.05 to 15 g./l. but from 20 to 30 g./l, the most negative

potential is attained in about 5 min. and afterwards the potential values register a fall till a stable value is attained. A comparison of the potential trend at 35 and 50°C show that at a particular hydrogen sulphide concentration the starting potential is more negative at 50 than at 35°C, but in about 15 to 30 min. the potential values are more or less tha same at both the temperatures and afterwards the potential values at 35°C remain more negative than those at 50°C; this trend continues till the end of each experiment.

It will be observed from Table 1 that weight-loss data do not exactly correspond to potential measurements. However, the general trend is that with an appreciable shift in the stable potential towards a less negative value the corrosion rate markedly decreases. In general, it can be stated that in solutions of hydrogen sulphide containing ammonia (34 g./l.) at temperatures upto 50°C the corrosion rate will be very low when the electrode potential of mild steel is not more negative than the value of —600 mV Vs Sat. Cal. electrode. It is further observed that at 35°C in the range of hydrogen sulphide concentrations 0.1 to 1.5 g./l. though the starting potentials are less than —600 mV yet the corrosion rates are widely different with different hydrogen sulphide concentrations. At 50°C also in the range of hydrogen sulphide concentration 0.1 to 0.5 g./l. the starting potentials are less than —600 mV and the stable potential values are about —1000 mV but here again the corrosion rates show wide variance.

These results clearly indicate that potential values are not indicative of the actual corrosion rate under all conditions and some other factors also play part, though the potential behaviour has thrown some light on the corrosion processes taking place in the hydogen sulphide-ammonia media. For a particular hydrogen sulphide concentration the more negative starting potential at 50°C than at 35°C might be indicative of a higher initial corrosion rate at the former temperature but within 15 to 30 min. the potentials at both the temperatures attain the same value and afterwards these at 50°C continue to be slightly less negative than those at 35°C. This also suggests that some factors other than potential values also determine the corrosion rate.

A good correlation exists between the corrosion rate and the nature of the corrosion product formed. Where the product is thick and non-adherent, there is a marked increase in the corrosion rate when the temperature is increased from 35 to 50°C. Whereas in most cases where the corrosion product is thin and adherent, the increase in corrosion rate with temperature is very small. Thus, the lack of exact parallelism between the potentials and the corrosion rates at 35 and 50°C might be due to the different types of corrosion products which get superimposed and introduce a rate-controlling barrier for the ions, and the reaction becomes diffusion-controlled.

The marked changes in electrode potential with changes in hydrogen sulphide concentration cannot be explained as due to the changes in pH, as in the present case the pH of the solutions lay between 10.5-11.0. Meyer et al[9] have clearly stated that the nature of sulphide film introduces a rate controlling barrier and affects the corrosion rate. Gardner[11] has also stated that the overall reaction velocity is in the range expected for diffusional control. Shannon and Boggs[10], Greco and Wright[12], Sardisco et al[16], have all observed that the corrosion rate is controlled by the sulphide film. Sardisco and Pitts[18] have stated that the overall reaction is partly interface and partly diffusion-controlled. They are of the view that all the film components are formed initially but the rate at which each grew and the number of crystallites formed were probably different. This observation is in agreement with our findings, and the probable mechanism may be as follows: initially the potential is indicative of the corrosion rate but soon with the formation of the different types of sulphide film, the reaction becomes diffusion-controlled and the potential values and corrosion rate become somewhat dependent on the nature of the sulphide films.

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Optimization of Cobalt Molybdate Type Catalysts for Hydrodesulphurization of Petroleum Feedstock—Part II

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Several best path nickel-promoted cobalt molybdate catalyst samples have been prepared and tested for their velocity coefficient of hydro-desulphurization taking mercaptan in heptane solution as feedstock. The present work shows two optimum compositions, first at around 8.76 per cent CoO, 6.12 per cent MoO and 0.71 per cent NiO and second at around 21.3 per cent CoO, 8.38 per cent MoO_3 and 1.63 per cent NiO; the latter, however, is more difficult to prepare for technical reasons.

Introduction

Nickel-promoted and alumina-supported cobalt molybdate catalysts have CoO, MoO_3 and NiO as effective variable constituents. To find the optimum composition of this type of catalyst, effect on velocity coefficient of hydrodesulphurization taking ethylmercaptan as test sulphur compound per unit values of these constituents at the base level were determined as per statistical procedure of Box and Wilson[1] in Part I[2] of this paper. The values of effect on velocity coefficient per unit values of these constituents were found as 0.4175, 0.0375 and 0.3075 respectively. The base level of these constituents were chosen as 2.5, 5.0 and 0.25 per cent respectively and the unit values as 1, 2 and 0.1 per cent respectively.

Best paths have been indicated[2] as base level + (effect per unit) $\times$ (unit value) $\times$ N where N is any number. To get the optimum composition of catalyst, i.e. the optimum value of N, several best path catalyst samples have been prepared and tested for their velocity coefficient of hydrodesulphurization taking ethyl mercaptan in heptane solution as feedstock. The optimum composition would be known from the value of N for which velocity coefficient is maximum.

Experimental

The method of preparation of catalyst and its test procedure are the same as described in Part I of this paper.

Results

The kinetic data (Table 1) with different catalysts have been correlated in the same way as in Part I[2] of this paper, and the results of correlation have been shown (Table 2). To indicate the effect of composition on the velocity coefficient the results of correlation with ethyl mercaptan as test sulphur compound has been plotted against N (Fig. 1).

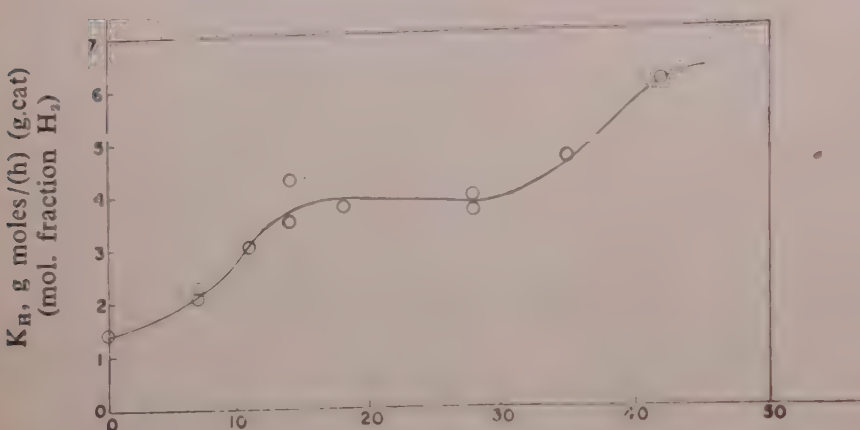

Fig. 1

TABLE 1—EXPERIMENTAL DATA (Representative Samples)

Run No.	F_H, g. moles H_2/h	F_{HC} g. moles Heptane/h	Temp., °C	Mercaptan in Heptane Feed, ppm. w/w	Per Cent Conversion
1	2	3	4	5	6
(a) Test Catalyst No. 2a [Composition (%) CoO 5.5, MoO_3 5.7, NiO 0.475; size: 4.9 mm.×9.0 mm.; wt. 50 g.] (Test Sulphur Compound—Ethyl Mercaptan)					
1.	0.38	0.79	227	11,800	39
3.	0.38	0.47	254	,,	75
5.	0.44	0.52	277	,,	81
7.	0.45	0.42	327	,,	91
9.	0.45	0.45	352	,,	95
11.	0.50	0.47	403	,,	97
(b) Test Catalyst No. 2b [Composition (%): CoO, 5.5, MoO_3 5.7, NiO 0.475; size: 8.65 mm×5.40 mm.; wt. 45 g.] (Test Sulphur Compound—Ethyl Mercaptan).					
1.	0.32	0.56	366	1639	88
5.	0.28	0.45	340	4209	92
12.	0.35	0.72	419	4209	92
14.	0.37	0.57	238	4270	73
16.	0.38	0.58	287	4270	79
18.	0.38	0.60	364	4270	84
20.	0.43	0.60	427	4270	90
29.	0.26	0.58	440	4270	89

TABLE 1—EXPERIMENTAL DATA *(Contd.)* (Representative Samples)

Run No.	F_H, g. moles H_2/h	F_{HC} g. moles Heptane/h	Temp., °C	Mercaptan in Heptane Feed, ppm. w/w	Per Cent Conversion
1	2	3	4	5	6
(c) Test Catalyst No. 3 [Composition (%) CoO 7.09, MoO_3 5.82, NiO 0.60; size: 5.1 mm×8.1 mm.; wt. 50 g.] (Test Sulphur Compound—Ethyl Mercaptan)					
1.	0.35	0.45	327	4900	99.3
3.	0.44	0.38	352	,,	99.2
5.	0.44	0.39	403	,,	98.3
7.	0.35	0.59	227	,,	76.5
9.	0.45	0.58	254	,,	76.0
11.	0.36	0.59	277	,,	84.2
(d) Test Catalyst No. 4a [Composition (%): CoO 8.34, MoO_3 6.04, NiO=0.69; size: 4.65 mm×8.80 mm; wt. 50 g.] (Test Sulphur Compound—Ethyl Mercaptan)					
1.	0.40	0.60	237	880	75.3
2.	0.40	0.54	287	,,	87.1
4.	0.45	0.72	403	,,	96.6
7.	0.46	0.72	262	1470	78.5
9.	0.49	0.77	312	,,	88.2
11.	0.50	0.72	364	1140	91.4
13.	0.58	0.67	442	,,	96.9
(e) Test Catalyst No. 4a [Composition (%): CoO 8.34, MoO_3 6.04, NiO 0.69.; size; 4.65 mm×8.80 mm.; wt. 50 g.] (Test Sulphur Compound—Thiophene)					
1.	0.42	0.55	240	3120	19.6
3.	0.42	0.55	290	,,	28.2
5.	0.44	0.55	340	,,	39.9
6.	0.44	0.54	340	,,	42.2
7.	0.44	0.51	390	,,	61.5
8.	0.42	0.51	390	,,	65.0
(f) Test Catalyst No. 4b [Composition (%): CoO 8.34; MoO_3 6.04, NiO 0.69; size 4.6 mm×9.1 mm.; wt 50 g.] (Test Sulphur Compound—Ethyl Mercaptan)					
5.	0.83	1.88	333	4400	86.4
9.	0.28	1.05	237	2200	67.3
11.	0.28	0.90	282	2200	88.8
13.	0.39	0.63	360	2200	97.6
14.	0.42	0.63	360	2200	98.3
15.	0.40	0.65	387	2200	98.4

TABLE 1—EXPERIMENTAL DATA *(Contd.)*
(Representative Samples)

Run No.	F_H, g. moles H_2/h	F_{HC} g. moles Heptane/h	Temp., °C	Mercaptan in Heptane Feed, ppm. w/w	Per Cent Conversion
1	2	3	4	5	6
(g) Test Catalyst No. 5 [Composition (%): CoO 10.2, MoO_3 6.34, NiO 0.82; size: 4.88 mm×10.50 mm.; wt 50g.] (Test Sulphur Compound—Ethyl Mercaptan)					
1.	0.41	0.49	227	3300	69.0
3.	0.46	0.55	254	,,	75.2
5.	0.55	0.43	277	,,	88.5
7.	0.42	0.42	327	,,	98.8
8.	0.46	0.97	352	,,	97.3
10.	0.38	0.89	403	,,	98.2
(h) Test Catalyst No. 6a [Composition (%) CoO 14.2, MoO_3 7.10, NiO 1.13; size 4.95 mm×7.85 mm.; wt 43.5 g.] (Test Sulphur Compound—Ethyl Mercaptan)					
1.	0.35	0.95	237	4300	57.0
3.	0.39	0.96	282	,,	65.5
5.	0.36	0.84	335	,,	77.2
7.	0.44	0.95	385	,,	83.2
9.	0.42	0.83	440	,,	88.6
12.	0.34	1.00	262	,,	62.6
14.	0.35	1.00	305	,,	72.2
16.	0.35	0.96	360	,,	80.0
18.	0.36	0.88	407	,,	87.5
(i) Test Catalyst No. 6b [Composition (%): CoO 14.18, MoO_3 7.08, NiO 1.13; size 5.50 mm×10.00 mm.; wt 50 g.] (Test Sulphur Compound—Ethyl Mercaptan)					
1.	0.42	0.55	232	880	46.5
2.	0.47	0.55	282	,,	72.3
4.	0.51	0.55	337	,,	91.8
6.	0.53	1.00	390	,,	82.7
8.	0.53	0.83	412	,,	92.8
10.	0.57	0.85	262	1700	79.5
12.	0.56	0.78	312	,,	85.6
14.	0.57	0.81	364	,,	93.4
(j) Test Catalyst No. 7 [Composition (%): CoO 17.11, MoO_3 7.60, NiO 1.35; size: 4.90 mm×11.10 mm.; wt 50 g.] (Test Sulphur Compound—Ethyl Mercaptan)					
1.	0.38	0.49	227	2600	89.4
3.	0.33	0.53	254	,,	94.6
5.	0.40	0.50	277	,,	99.3
7.	0.40	0.54	325	,,	99.4
9.	0.40	0.41	352	,,	99.2
11.	0.43	0.41	402	,,	99.2

TABLE 1—EXPERIMENTAL DATA *(Contd.)*
(Representative Samples)

Run No.	F_H, g. moles H_2/h	F_{HC}g. moles Heptane/h	Temp., °C	Mercaptan in Heptane Feed, ppm. w/w	Per Cent Conversion
1	2	3	4	5	6
(k) Test Catalyst No. 8 [Composition (%) CoO 20.0, MoO_3 8.15, NiO 1.57; size 5.6 mm×8.4 mm.; wt 47 g.] (Test Sulphur Compound—Ethyl Mercaptan)					
1.	0.50	0.50	232	3740	86.9
3.	0.48	0.58	282	,,	94.3
5.	0.47	0.58	332	,,	98.4
7.	0.53	0.85	387	4000	99.2
9.	0.55	0.72	437	,,	98.7
13.	0.51	1.01	264	,,	80.0
15.	0.54	0.97	305	,,	92.4
17.	0.51	0.93	372	,,	97.2
19.	0.54	0.97	407	,,	98.4
(l) Test Catalyst HDS C-49 (Size 3.0 mm×7.0 mm.; wt 50 g.) (Test Sulphur Compound—Ethyl Mercaptan)					
1.	0.45	0.61	215	3300	54.5
3.	0.43	0.52	252	,,	63.5
5.	0.43	0.50	284	,,	79.0
7.	0.47	0.61	333	,,	86.4
9.	0.50	0.57	365	,,	85.1
11.	0.56	0.77	415	,,	89.3

Fig. 1 shows that as N increases, the velocity coefficient increases to a maximum value at about N=15 (corresponding composition being CoO 8.76, MoO_3 6.12 and NiO 0.71%) and then remains constant between N=15 to 30 (N=30 stands for CoO 15.02, MoO_3 7.25 and NiO 1.17%) and then again the velocity coefficient increases with N in the range of N=30-42. A second maximum appears at about N=45 for which composition is CoO 21.3, MoO_3 8.38% and NiO 1.63 per cent.

Considering technical difficulties and cost of preparation of catalyst corresponding to higher values of N it is believed that for hydrodesulphurization of mercaptan type of organic sulphur compound a catalyst corresponding to N=15 may prove to be an optimum catalyst for commercial purposes. For hydrodesulphurization of ethyl mercaptan in heptane solution the velocity coefficient of a catalyst has been found as 3.9 for N=15 and 6.05 for N=42 compared to 1.29 for a commercial sample of catalyst (HDSC-49).

TABLE 2—RESULTS OF CORRELATION OF KINETIC DATA

Test Catalyst No.	N (any Number)	Composition, wt % CoO	MoO_3	NiO	E, cal/g. (mol.)	K_H, g. moles/(h) (g. cat) (mol fraction H_2)	Size, diam × height mm × mm.	L, pore length, mm.	K_H on $\bar{L}$ =1.5 mm
					(a) Test Sulphur Compound—Ethyl Mercaptan				
I	0	2.5	5.0	0.25	3974	1.35	6×9	1.591	1.43
2a	7	5.5	5.7	0.475	-do-	2.46	4.9×9	1.365	2.24
2b	7	5.5	5.7	0.475	-do-	2.22	5.4×8.65	1.445	2.14
3	11	7.09	5.82	0.60	-do-	3.34	5.1×8.1	1.370	3.05
4a	14	8.34	6.04	0.69	-do-	4.05	4.65×8.8	1.300	3.52
4b	14	8.34	6.04	0.69	-do-	4.95	4.6×9.1	1.310	4.32
5	18	10.2	6.34	0.82	-do-	4.05	4.88×10.5	1.400	3.78
6a	28	14.2	7.10	1.13	-do-	4.48	4.95×7.85	1.325	3.96
6b	28	14.2	7.10	1.13	-do-	3.64	5.5×10	1.525	3.70
7	35	17.10	7.60	1.35	-do-	4.95	4.9×11.1	1.420	4.63
8	42	20.0	8.15	1.57	-do-	6.1	5.6×8.4	1.487	6.05
*HDS-C-49	—	—	—	—	-do-	2.23	3×7	0.87	1.29
					(b) Test Sulphur Compound—Thiophene				
1	0	2.5	5.0	0.25	4170	0.55	6×9	1.591	0.583
4a	14	8.34	6.04	0.69	3974	0.67	4.65×8.80	1.300	0.581

The results of correlation with thiophene as test sulphur compound show that the velocity coefficient of hydrodesulphurization with thiophenic sulphur compound is independent of N or, in other words, does not increase with increase in CoO and NiO concentrations. It will be interesting to compare the results of these studies with those by Andrews[3] who has made a detailed investigation into the effects of composition on the catalytic activity of alumina-supported cobalt molybdate catalyst.

Andrews[3] has used straight-run Middle East diesel oil of boiling range 480-700°F containing 2 per cent of combined sulphur and has found an optimum composition of catalyst at around CoO 5.5 and MoO_3 16 per cent. Sulphur compounds in crude oil residues boiling above 200°C are almost entirely cyclic in nature and are for the most part condensed thiophenes of almost every series[4]. Andrews' work thus shows that for hydrodesulphurization of cyclic thiophenic type of sulphur compound increase in MoO_3 concentration in catalyst is more effective than that of CoO. Our work[5,6] also shows that for alumina-supported nickel promoted cobalt molybdate type of catalyst increase in CoO content beyond 2.5 per cent is of very little use for hydrodesulphurization of thiophene whereas for hydrodesulphurization of mercaptan CoO is useful even upto 20 per cent.

Nomenclature

E = energy of activation, cal./g. mol

K_H = velocity coefficient g. mole/(h) (g.cat.) (Mol. fraction H_2)

$\bar{L}$ = pore length, mm.

N = any number

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Physical Studies of Rock Phosphate

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A study has been made on the mineralogical composition and physical characteristics of several varieties of rock phosphate of the North African and the Pacific coast deposits—which are used extensively for the manufacture of phosphatic fertilizers,—with x-ray and differential thermal analyses. Apatite group of minerals has been found to be the major constituent of all the rocks examined in the present case. Besides fluorapatite, the evidence of the presence of carbonatoapatite has been detected in all cases. Other minor phases detected are calcite and sulphide in all the samples. Further, on heating these samples upto 900°C, the structure of their apatites remains essentially similar to that of unheated samples.

Rock phosphate is used extensively as raw material in the manufacture of phosphatic fertilizers. Their chemical and physical properties, however, vary with their origin, mode of deposition as well as mineralogical composition. Known phosphate deposits of economic importance are mainly located in the U.S.A., North Africa, U.A.R., Russia, France, Spain, Sweden, and the Pacific islands. Extensive studies on the American rock phosphates regarding their physical and chemical properties, crystal phase composition, size and reactivity have been made by a numbers of worker[1–3]. But very little is known about the characteristics of the North African deposits[4,5].

Rock phosphates constitute minerals mainly of the apatite group. Besides fluorapatite, which is most abundant and widely distributed crystalline phosphate present in rock phosphates, other phosphates like hydroxy- and carbonatoapatite are also found to be associated with the rocks.

In fluorapatite—the formula $3Ca_3(PO_4)_2CaF_2$ is usually ascribed to this mineral—the fluorine content is 3.77 per cent but this may be replaced partially by groups like OH, Cl, oxygen and carbon dioxide. The effect of this substitution is accompanied by a change in the unit cell dimensions. The x-ray diffraction patterns are in general similar to each other but there is a minor difference in the intensity maximum of some of their lines. Recent studies[5] have shown that refined x-ray procedures are available for characterization of these minerals. Because of the similarity of x-ray diffraction patterns of substituted apatites, a very precise measurement of intensity of certain reflections and an accurate spacing determination will be required in order to distinguish them.

Very little is known about the differential thermal analysis of these rock phosphates. It may be mentioned here that carbonatoapatite admixed with free calcite has been identified by DTA[6], with the help of the peaks that appeared separately in the region 700-750°C and 800-850°C. But the identification of free calcite present in the rock phosphates containing carbonatoapatite is still now a highly controversial issue. Considering these, an attempt has been made to examine the mineralogical composition and physical characteristics of some rock phosphates of North African and Pacific coast deposits with the aid of x-ray and DTA techniques.

Experimental

Experimental Specimens (1) *Natural Apatite:* Representative samples of four varieties of rock phosphates, viz. from Jordan, Tunisia, Morocco and Makatea, constitute the present investigation; amongst them, Jordan and Tunisian varieties were collected from the Superphosphate Factory, Sindri,

The rocks were chemically analysed (Table 1). P_2O_5 and fluorine contents of these rocks are variable within the range 30.3-37.8 as well as 2.6-4.86 per cent respectively. All these rocks also contain carbon dioxide and sulphide. They are in the range of 1.3-6.07 and trace to 2.52 per cent (as SO_3) respectively.

TABLE 1—CHEMICAL ANALYSIS OF DIFFERENT ROCK PHOSPHATES, % by wt.

Constituents	Tunisia	Jordan	Morocco	Makatea (Pacific coast)
CaO	49.66	52.40	50.03	51.65
P_2O_5	30.30	34.45	32.34	37.80
F_2	2.85	4.86	2.60	2.79
CO_2	6.07	4.75	5.03	1.30
SO_3	2.52	Trace	1.28	0.17
SiO_2	2.60	2.50	2.09	0.10
Fe_2O_3	0.87	0.22	0.66	1.14
Al_2O_3	—	—	—	—
MgO	0.62	—	—	—
Undetermined	4.51	0.82	5.97	5.05
	100.00	100.00	100.00	100.00

(2) *Synthetic Apatite* (*a*) *Hydroxyapatite:* This apatite was prepared by following the method of Winand[7]. Hydroxyapatite was prepared by double decomposition of hot and concentrated solution of calcium chloride and potassium dihydrogen phosphate. The precipitate was washed with distilled water and dried in oven at 95°C.

(*b*) *Fluorapatite:* This apatite was prepared by following the method of Maslennikov et al.[8] Artificial fluorapatite was obtained by a careful mixing of stoichiometric amounts of tricalcium phosphate and calcium fluoride and calcination of the mixture at 900°C for about 4 hours.

(*c*) *Carbonatoapatite:* The synthesis was carried out by following the method described by Romo[9]. Calcium carbonate was treated with potassium dihydrogen phosphate in the presence of an excess alkali. The solid

TABLE 2A—X-RAY STUDY OF ROCK PHOSPHATES

Jordan		Tunisia		Morocco		Makatea (Pacific Coast)		ASTM Standard X-ray Data on							
								Hydroxy-apatite[9]		Carbonato-apatite		Fluorapatite		Calcite	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
3.48	m	3.48	m	3.48	m	3.47	mw	3.44	40	3.86	2.6	3.44	20	3.04	100
3.21	w	3.20	w	3.22	w	3.21	w	3.11	8	3.418	4.0	3.07	30	2.845	3
3.07	w	3.08	w	3.08	w	3.07	w	3.08	30	3.120	1.2	2.81	100	2.495	14
2.81	vs	2.81	vs	2.81	vs	2.81	vs	2.81	100	3.048	2.0	2.71	60	2.285	18
2.71	s	2.71	s	2.71	s	2.71	s	2.78	60	2.796	10.0	2.63	30	2.095	18
2.65	m	2.64	m	2.65	vw	2.63	m	2.72	60	2.771	7.4	2.53	5	1.927	5
2.55	vvw	2.55	vvw	2.55	vvw	2.55	vvw	2.62	8	2.698	3.8	2.49	5	1.913	17
2.26	m	2.26	m	2.25	m	2.26	m	2.27	16	2.629	2.2	2.30	5	1.875	17
2.15	w	2.15	vw	2.15	vw	2.14	vw	2.13	4	2.398	2.6	2.26	20	1.626	4
2.01	vw	2.07	vw	2.08	vvw	2.07	vvw	2.06	4	2.250	1.8	1.04	10	1.604	8
1.96	m	2.02	vvw	2.02	vw	2.01	vw	1.94	20	2.141	1.0	2.06	10	1.525	5
1.85	s	1.96	m	1.96	m	1.95	m	1.84	20	1.956	0.6	2.03	5	1.518	4
1.81	w	1.90	vw	1.90	vw	1.90	vw	1.71	16	1.941	2.3	2.00	5	1.510	3
1.75	w	1.85	s	1.85	s	1.85	s	1.45	8	1.887	1.4	1.95	40	1.473	2
1.65	vw	1.81	vw	1.81	w	1.81	w	1.31	8	1.835	2.3	1.89	10	1.440	5
1.62	vw	1.74	w	1.74	w	1.76	w	1.24	4	1.797	1.4	1.84	60	1.422	3
1.55	vw	1.65	vw	1.65	vw	1.74	w	1.11	8	1.772	1.0	1.80	30	1.356	1
1.52	vw	1.54	vw	1.51	vw	1.65	vw			1.742	0.5	1.77	30	1.399	2
1.49	w	1.52	vw	1.48	w	1.62	vw			1.725	0.5	1.75	30	1.297	2
1.44	vw	1.48	w			1.54	vw			1.698	1.6	1.72	30	1.284	1
		1.44	vw			1.51	vw			1.639	0.6	1.64	30	1.247	1
						1.48	vw			1.527	1.4	1.61	5	1.235	2
						1.46	vw			1.460	0.5	1.54	5	1.800	3
						1.44	vw			1.454	1.0	1.52	5	1.153	3
										1.448	1.2	1.50	10		
												1.47	20		
												1.46	10		
												1.45	10		
												1.43	10		

TABLE 2B—INTENSITY MEASUREMENTS OF ROCK PHOSPHATES

Jordan		Tunisia		Morocco		Makatea (Pacific coast)	
dÅ	I, counts/sec.	dÅ	I, counts/sec.	dÅ	I, counts/sec.	dÅ	I, counts/sec.
3.48	400	3.48	400	3.48	400	3.48	250
2.81	700	2.81	700	2.81	700	2.81	700
2.71	500	2.71	500	2.71	500	2.71	500
1.85	400	1.85	400	1.85	400	1.85	400

TABLE 3—UNIT CELL DIMENSIONS OF SOME APATITES

Apatites	a, Å	c, Å	References
OH -apatite	9.422	6.883	11
F -apatite	9.372	6.888	12
CO_3 -apatite	9.366	6.932	13
Cl -apatite	9.484	6.848	14

TABLE 4

Carbonatoapatite		Fluorapatite		Hydroxyapatite	
dÅ	I	dÅ	I	dÅ	I
2.82	100	2.81	100	2.81	100
2.71	90	2.71	60	2.78	60
3.44	80	1.84	60	2.72	60
1.84	20	3.44	20	3.44	40

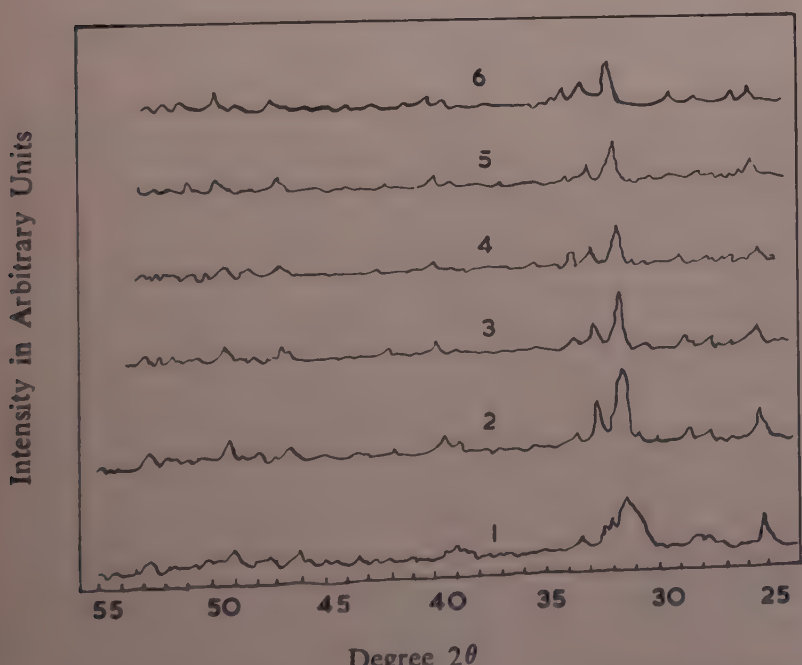

Fig. 1—Diffractometer Curves for Synthetic and Natural Apatite.

1. Hydroxy Apatite
2. Carbonato Apatite
3. Morocco Rock Phosphate
4. Tunisia Rock Phosphate
5. Makatea Rock Phosphate
6. Jordan Rock Phosphate

phase is washed with distilled water and ethyl alcohol. Finally, the alkali-free solid phase was dried at 95°C.

X-ray Study: X-ray diffraction patterns of the samples were obtained in RKD Camera (Cassette diameter 57.3 mm.) with CuKα radiation using nickel filter at 30 KV and 20 mA giving 6 hours of exposure to each sample. The samples were also run on the Philips X-ray diffractometer PW 1050/51. The diffraction angles were obtained from charts recorded at a scanning speed 1°/min 2θ, with time constant 4 seconds using divergence slit 1°, scatter slit 1° and receiving slit 0.2 mm. A standard silicon, supplied by Philips, was also studied in order to correct the observed 'd'-values if any. The diffraction patterns of the samples heated to 900°C for 6 hours, were also taken and d-values calculated. Their x-ray data are similar to those of the unheated samples. As such they are not presented here. The interplaner distances of the lattices were calculated from the measurement of x-ray diffraction pattern with maximum accuracy. The intensities of some of the diffraction lines were evaluated from the counts at their peak position. The identification of crystalline phase was made by the usual method of Hanawalt et al[10].

DTA Study: The instrument used was of Linsies Model, fully automatic DTA unit, the thermocouple of Pt/Pt-Rh and the sample holders were of thin Pt-cylinder. It was designed to run three samples at a time. The rate of heating was controlled at 10°C/min. by a programme controller. α-alumina was used as a reference substance. Identification of the components was made by the peaks that appeared in the DTA curve of the samples.

Results

A critical analysis of the x-ray diffraction data reveals that the rocks examined are similar to fluorapatite mainly. The presence of carbonatoapatite is also detected as is evident from the variation of intensity of some of the 'd' spacings in their x-ray pattern (Tables 2-4 and Fig. 1).

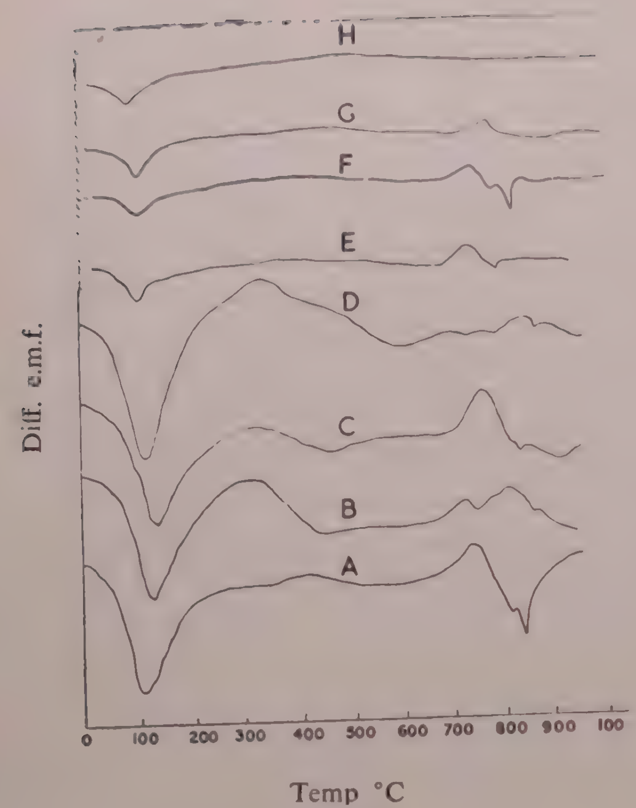

Fig. 2.

A Jordan
B Tunisia
C Morocco
D Makatea
E Carbonato Apatite Synthetic
F E+2% Calcite
G Hydroxy Apatite Synthetic
H Fluoro Apatite Synthetic

A critical analysis of DTA thermograms of the samples (Fig. 2) reveals both endo- and exothermic peaks. In all samples, the endothermic peaks are found in the region of 110-120°C, 780-810°C and 830-850°C, while one exothermic peak is found in the region 725-750°C in each case (Table 5). In addition, there is one exothermic bulge in the region of 320-420°C. The thermograms of all these samples were compared with those of the synthetic ones (Fig. 2).

Discussion

The x-ray diffraction data of the samples reveal that they consist of fluorapatite mainly. But from the intensity maximum, the evidence of carbonatoapatite has also been detected in all the samples and that of Makatea variety seems to be less substituted by carbonate in its apatite lattice [vide Table 2 (A & B)].

The DTA thermograms of these samples (Fig. 2) are, in general, similar to each other indicating thereby the presence of similar minerals in all samples. The presence of endothermic peaks in the region 110-120°C in their thermograms is due to mechanically adsorbed moisture in the samples. The appearence of a bulge in the region 320-420°C may be attributed to the sulphides which have been detected by chemical test also. The intensity of this peak is maximum in the Tunisian variety whose sulphur trioxide content (Table 1) is the highest. Further, this peak intensity of the samples varies in the following order, Morocco>Makatea>Jordan. This observation is quite in conformity with the chemical analysis, (of SO_3 content, vide Table 1).

The appearance of exothermic peak in all the rocks around the region of 730-750°C is similar to that of synthetic hydroxyapatite and carbonatoapatite (Fig. 2). It is interesting to mention here that in case of synthetic fluorapatite, this peak is absent and the DTA thermogram is featureless. Again synthetic hydroxy and carbonatoapatite differ among themselves in their DTA diagram by one weak endothermic peak at 770-810°C, which in case of carbonatoapatite is immediately followed by the above exothermic peak. These two peaks are also found in the rock phosphates and as such it may be concluded that carbonatoapatite is present as one of the phases of these samples. The endothermic peak in the region of 830-850°C in case of rock phosphates is similar to that of mechanically mixed synthetic carbonatoapatite with 2 per cent calcite (Fig. 2). This peak, therefore, indicates free calcite in the natural samples. It is worthwhile to mention here that x-ray data (Table 2, Fig. 1). do not give any idea of the presence of this calcite. This may possibly be due to its small amount in the rock phosphates and/or poorly defined crystalline nature. This observation indicates that presence of free calcite in rock phosphates containing carbonatoapatite may be identified by DTA.

Again, the exothermic peak in the region of 730-760°C in case of the synthetic carbonate and hydroxyapatite

TABLE 5—Peak Temperature of Rock Phosphates & Synthetic Apatites

Sample	Endothermic	Exothermic
Synthetic Apatites		
Fluorapatite	110 Weak	—
Hydroxyapatite	110 Strong	750-760 medium
Carbonatoapatite	110 Weak	730 Strong
	770 Weak	
Rock Phosphates		
Jordan	110 Strong	400-420 bulge
	810 Weak	735 medium
	840 Medium	
Tunisia	120 Strong	350 bulge
	780 Weak bulge	725 medium
	850 Weak	
Morocco	120 Strong	300-400 bulge
	780 Weak	730 medium
	830 Weak	
Makatea	110 Strong	300-400 bulge
(Pacific Coast)	780 Weak	740-750 medium
	840 Weak	

indicates that the structural change associated with this peak is similar in both the cases. Further, it is known that when hydroxyapatite is heated upto 900°C[15], oxyapatite is formed, having a structure similar to that of fluorapatite. Similar is the case with carbonatoapatite also as is evident from the x-ray data of both natural rock phosphates as well as synthetic carbonate and hydroxyapatite before and after heating at 900°C.

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Infra-Red Absorption Study of Urea-Humic Acids Complex

By

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An attempt has been made to study the mechanism of interaction between urea and soil humic acids by infra-red spectra. It has been suggested that the complex formation between urea and humic acids occurs through nitrogen of urea and oxygen of the carboxylate ion present in humic acids. Further, it has been presumed that the stability of the urea-humic acid complex is due to the moderately strong hydrogen bond formation.

Both urea and humus have long been used as fertilizers. But, very recently, the suitability of urea and humic acid mixtures as fertilizers has received much attention. Nakajima and coworkers[1,2] prepared both powdered and granulated urea-humate from a mixture of urea and humic acids, but nothing has been mentioned about its chemical nature.

Dragunova and coworkers[3] presumed that the solubility of humic acid in 5M urea is due to an addition reaction of humic acids, urea and water. Pal and Banerjee[4] observed that urea forms an addition complex with humic acid resulting in a decrease in the exchange capacity and increase in pH. Ghosh, Gupta and Pal[5] observed from the ESR spectrum of humic acid, the existence of a stable free radical and presumed the role of the free radical in the urea-humic acids interaction. However, the nature of the free radical taking part in the interaction between the urea and humic acids and the inner structure of this addition product have not yet been determined.

The knowledge of the nature of bonding between urea and humic acids and its stability may contribute to the understanding of its suitability as a fertilizer. This may also help to clarify the role played by humic. acids in the retention of urea when the latter is applied as a fertilizer to a soil containing an appreciable amount

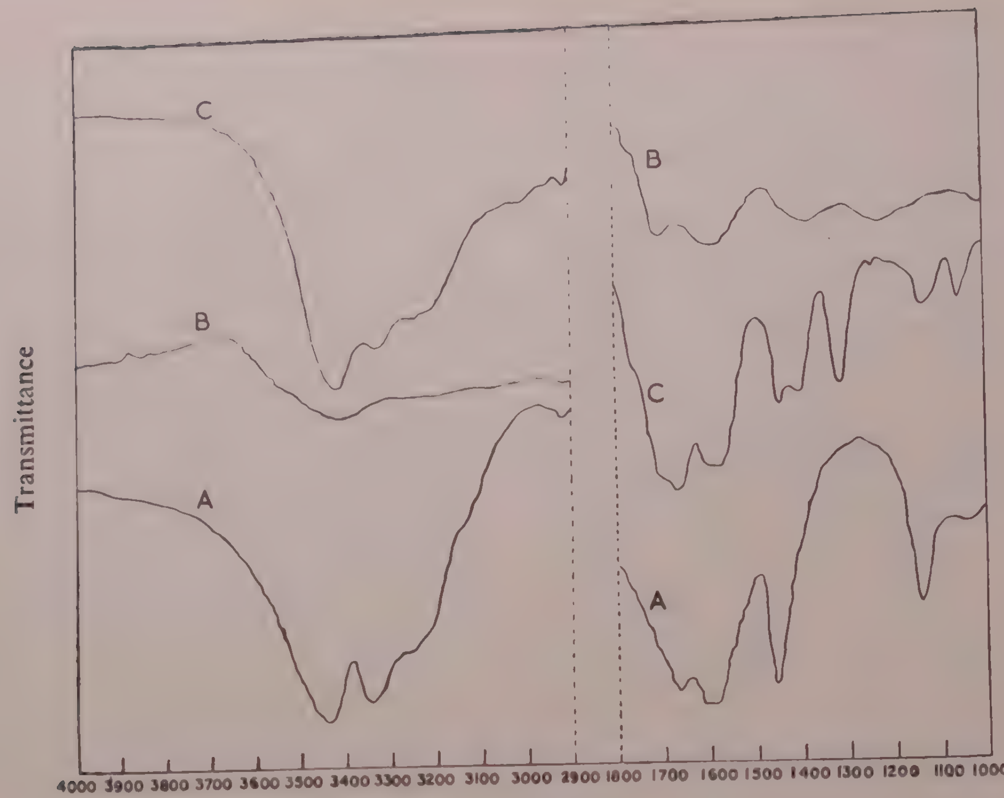

Fig. 1—Infrared Spectra.
A—Urea, B—Humic Acids, C—Urea Humic Acid Complex.

of organic matter. In view of these, the object of this study is mainly to understand the nature of interaction between urea and humic acids.

Experimental

Preparation of the Urea-Humic Acids Complex. The humus was extracted from a sample of black cotton soil (Amaravati, Maharashtra) and from it humic acid (containing hematomelanic acid) was prepared finally by electrodialysis as described earlier[4]. Humic acid was diluted to a 0.264 per cent (w/v) suspension. The pH* of the suspension was 3.62.

20. c.c. of the humic acids suspension was mixed with 20 c.c. of 10 M urea in a 250 c.c. Pyrex conical flask and the mixture kept in a thermostat at 27°C for 27 days. The pH of the urea-humic acids mixture after 27 days was found to be 8.50. The mixture was dried in vacuo and the solid mass was analyzed by IR.

Absorption Measurements: All the samples, viz. urea, humic acids and urea-humic acid complex, were studied in the solid phase by KBr disc technique with the Perkin Elmer Infra-red dual grating spectrophotometer, Model 421.

KBr pellets were prepared following a nearly similar procedure described by Ingebrigtson and coworkers[6] in an earlier paper[7]. The diameter of the pellet was 13 mm. having a thickness of 1 mm. The spectra was recorded fróm 2.5 to 18 μ using strip chart recorder and the scanning speed was 17 minutes for the full range.

*Measured by a Philips PR 9403 pH meter

Results

The absorption curves of urea, humic acid and urea-humic acid complex are reproduced in Fig. 1.

Urea: The spectra of urea (Fig. 1A) obtained in this study is quite similar to those reported by other workers,[8–11] and hence the assignments have been made accordingly. The wave numbers (cm.$^{-1}$) of the absorption maxima together with their assignments are given in Table 1.

Humic Acids: The infra-red spectra of the humic acid is complicated and the bands observed in the present investigation (Table 1) are in general agreement with those reported by others[12–14]. One interesting feature of the IR spectra of KBr pellets of the resultant humic acids (Fig. 1B) is the presence of absorption bands at 1600 and 1393 cm.$^{-1}$, which may be due to the presence of carboxylate ions. Since, humic acid is a relatively weak acid, it is not expected to be readily ionized. But Asfeld and coworkers[15,16] in their studies on humic acids by the IR method have shown the existence of both H_3O^+ and COO^- in humic acids. It may be mentioned here that ESR spectrum study[5] of the present sample also shows the presence of free radical. Absorp-

tion bands are also present at 1710 and 1230^{-1}, which may be indicative of the presence of non-ionized carboxyl groups.

Interaction of Urea-Humic Acids: The striking features of the IR spectrum (Fig. 1C) of urea-humic acids complex compared to those of pure urea and humic acids are the occurrence of (i) a shoulder at about 1730 $cm.^{-1}$ and (ii) a new band at 1322 $cm.^{-1}$. Penland and coworkers[11] in their studies on the urea complexes reported that when urea is coordinated through the nitrogen atom, there is a shift in the 6μ region of urea and a decrease in the C: N stretching frequency to about 1400 $cm.^{-1}$. They also observed that the frequency of NH_2 bending vibration of pure urea at 1603 $cm.^{-1}$ falls to 1585 to 1590 cm^{-1}, and this they assigned to coordinated NH_2 bending vibration. Following Penland's observation, the band at 1730 $cm.^{-1}$, has been assigned to C:O vibration. The new band at 1322 $cm.^{-1}$, has been attributed to C:N stretching of coordinated urea. This result shows that there is increase in the double bond character of oxygen to carbon bond and single bond character of nitrogen to carbon bond of the structure of urea indicating the coordination of urea to humic acid through the nitrogen atom of urea molecule. The assignments of other bands are shown in Table 1. Because of the complexity of the urea-humic acid spectra and the overlapping between the absorption bands of urea and that of humic acid in the 1600 $cm.^{-1}$ region, it was not possible to resolve the peaks associated with coordinated NH_2 bending, since the band at 1590 cm^{-1}. which may be thought of to be due to shifted NH_2 bending frequency of pure urea may also arise from free humic acid.

TABLE 1—Absorption Maxima (cm^{-1}) Observed for Urea, Humic acids and Urea-Humic Acids Complex and Their Assignments

Urea†	Urea*	Assignments	Humic Acid	Assignments**	Urea-humic acid complex	Assignments
3445 (S)	3436 (S)	$\nu(NH_2)$ assym. stretching	3420 (M, VBr)	H-bonded OH	3425 (S)	Free NH_2
3347 (S)	3347 (S)	$\nu(NH_2)$ symm. stretching			3332 (S)	
					3245 (MS)	
3255 (MS)	3255 (W)	combinations or overtones			3210 (MS)	
3220 (M)			2920 (VW)	aliphatic CH stretching	2915 (W)	
2928 (W)			1772 (VW,Sh)	anhydrite (?)		
					1730 (W, Sh)	ν(CO) Coordinated
			1710 (W, Br)	Carboxyl group	1710 (W, Sh)	
1675 (S)	1686 (S)	$\delta(NH_2)$ bending & (CO) stretching			1680 (S)	ν(CO) stretching & (NH) bending uncoordinated.
1607 (S)	1606 (S)	$\delta(NH_2)$ bending, A symmetry type++	1600 (MS)		1590 (S, Br)	
				Carboxylate ions	1457 (MS)	ν(CN) uncoordinated
1463 (S)	1468 (S)	ν(CN) stretching, B symmetry types	1393 (MS,Br)		1390 (MS)	
					1322 (MS)	ν(CN) coordinated
			1235 (W, Br)	Carboxyl group		
1152 (S)	1153 (M)	$\delta(NH_2)$ rocking, A & B symmetry type			1145 (W)	Free NH_2 rocking or coordinated NH_2
1050 (MS, Br)	1064 (W)				1069 (W)	Wagging vibration
			1025 (VW, Br)	O-H deformation of primary alchols and/or of C-O stretching ethers.		

S Strong, MS medium strong, M Medium, W weak, Br broad, Sh shoulder, Vbr very broad.

†KBr pellet spectrum obtained by the authors; assignments made in accordance with observation by Stewart[8], Yamaguchi, et al[9] and Spinner[10].

*taken from Stewart[8]

++symmetric species (non-degenerate) about the principal axis.

**assignments made in accordance with observations by other workers[12-14].

Discussion

It can be seen from the spectra of urea-humic acid complex (Fig. 1C) and also from Table 1 that there is a decrease in the NH stretching frequency and the appearance of a band at about 1730 $cm.^{-1}$ This result indicates that probably a weak hydrogen bond is formed between NH_2 groups of urea and oxygen of the carboxylate ion of humic acid. Sutherland[17] has indicated that whenever hydrogen bond is formed by association of the NH_2 groups with ketonic groups forming N-H. . . O=C links, the main NH absorption occurs near 3320-3240 $cm.^{-1}$ A much smaller decrease in the NH stretching frequency has been noted by Mitsui and Takatoh[18] in urea-montmorillonite system and reported that the NH stretching frequencies at 3500 and 3400 $cm.^{-1}$ for pure urea and at 3490 and 3400 $cm.^{-1}$ for urea in bentonite. Further, the carbonyl absorptions of amides containing the group CO-NH-CO appear as two bands in the regions 1790-1720 $cm.^{-1}$ and 1710-1670 $cm.^{-1}$, the first of these is assigned to the carbonyl group hydrogen bonded to NH and second is assigned to the normal carbonyl absorption. Consequently, the mechanism of bonding of urea in humic acid may be assumed to be similar to that of an amide and therefore contains NH . . . O=C link. However, this does not rule out the possibility of a dipolar interaction mechanism for such a case instead of a conventional type of hydrogen bond in view of the large shift in the carbonyl vibration as compared to the small shift in the NH stretching frequency. Cannon[19] reported a similar mechanism in connection with the study on the associated amides.

In the earlier investigation[4] on the urea-humic acids complex it has been observed that when urea is added to humic acid, the pH of the latter increases and its exchange capacity decreases with the complex formation, which indicates the urea-humic acid linkage is quite stable. Further, the increase of pH of the urea-humic acids mixture suggests that COOH groups, which are responsible for the observed H-ion concentration of humic acid, are gradually used up due to the complex formation with urea.

The chemical evidence stated above also supports the view of the hydrogen bond formation which lends stability to the urea-humic acid complex and the amide structure of the complex containing —NH . . . O=C- link formed by interaction of the oxygen of the free carboxylate ion present in the humic acid with the amino group of urea.

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Design of Model 33 kV Single Circuit Line With Suspension Strings

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The transmission lines upto 33 kV are normally constructed on pin insulators but in regions where birdage trouble is experienced it is much safer to use suspension strings. A braced channel pole has been designed to carry the line in zig-zag formation. Mention has been made about the care to be taken to maintain the strength in the longitudinal direction as one quarter the strength in the transverse direction to fulfil the condition specified in the Indian Electricity Rules. The braced channel pole is designed as an intermediate structure. At large angle and dead-end locations, rail or steel tubular poles, single or as H pole, will have to be used depending upon the strength required at each location.

The properly designed and erected transmission line can safely be guaranteed to give hazard-free service. There is therefore hardly any justification to be prejudiced and say that it is safer to go in for underground cables ratner than use overhead lines to feed important loads. In fact, long underground cables can prove to be more hazardous than overhead lines if their paying out and laying in ground is not carefully and properly done or they have some inherent manufacturing defects. On overhead lines one could exercise better supervision and have efficient control. Therefore, hazard-free transmission and distribution lines will always serve well and save the equipment and machinery from severe breakdowns and damage.

The birdage trouble is a potential hazard on high voltage transmission and distribution lines. Usually, such lines are erected on pin insulators with wooden or sometimes steel cross arms, the latter being more prone to birdage. In 1962 the author discovered that the 33 kV lines from the Delhi Grid Substation (P.S.E.B.) were giving immense trouble. There were breakdowns of conductors practically every alternate day, which not only resulted in the discontinuity of supply to important load centres, but also affected adversely the life of the plant and machinery installed in the Substation. All the equipment, such as transformers, circuit-breakers and synchronous condensers, were working at a great strain as they were frequently responsible for the severest short circuit. Besides such an unpleasant atmosphere, the entire electrical equipment was in a great danger. Under such conditions the author was asked to design a model 33 kV single circuit line which should be economical at the same time immune, as far as possible, from birdage and other line hazards. What followed thereafter was a design of a model single circuit 33 kV line which is now operating between Delhi Grid Substation and Bahadurgarh. This line traverses through a countryside experiencing big floods which are harmful to the pole foundations if not designed and erected properly. The single pole foundation has been discussed at length elsewhere[1]. It is, however, important to mention that pole foundation has to be properly coordinated with the superstructure with all the wayside hurdles having been taken into account. The foundation may need be just of ordinary, concrete, raised plinth or even of well type depending upon the conditions obtaining at the various sites.

The line is constructed with three 7/0.136″ stranded copper conductors placed in a zig-zag formation (Fig. 1) Single earth-wire 7/14 SWG,* G.S.S.** is erected on top of the conductors. The provision is also kept for future telephone line if considered necessary with 2 numbers of 10 SWG cadmium copper conductors. The maximum span is kept 400 feet. The wind pressure of the region is taken as 15 lbs/sq.ft. acting on a full projected area

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*Standard Wire Gauge.

**Galvanized Steel Stranded.

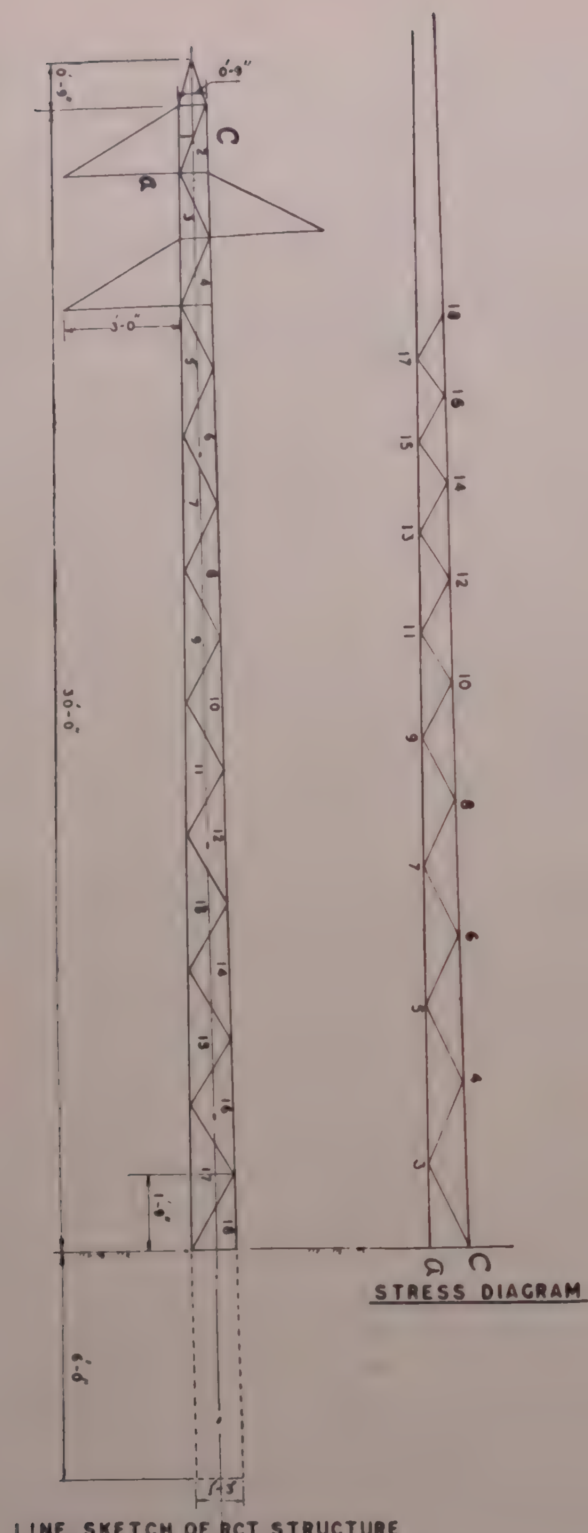


Fig. 1—Line Diagram of RCT structure.

of the conductors and earth wire and full surface area of the structure. The leeward side effect has been ignored as the base of the structure being too small there is no likelihood of any wind pressure acting on the shielded side of the structure. There had been incidents when the transmission and distribution lines in this region had fallen flat when squalls followed heavy rains and weak foundations could not resist the overturning moment due to heavy windage. All past studies and experience were kept in view while embarking on the present design study.

TABLE 1A—Calculations for the Design of the RCT Structure

Working Load Calculations

Conductor size	=	7/.136″ stranded copper
Earth wire size	=	7/14 GSS
Dia of 7/.136″ conductor	=	0.408 inches.
Wind pressure	=	15 lbs/sq.ft.
Assumed span	=	400

$$\frac{0.408\times15\times400}{12}\left(24\tfrac{3}{4}+26\tfrac{1}{2}+28\tfrac{1}{4}\right)$$

$$+0.25\times\frac{15}{12}\times400\times30=W\times29$$

where W is the load acting one ft. below the top of the structure.

$$\text{or } 5\times40.8\times\frac{159}{2}+0.25\times15000=W\times29.$$

$$\text{or } 102.0\times159+0.25\times15000=W\times29$$

$$\text{or } 16218+3750 = W\times29$$

$$\text{or } W=\frac{19968}{29} = 688 \text{ lbs. working load.}$$

say 700 lbs.

So the structure will be designed with a working load of 800 lbs. applied at 1 ft below top.

The structure which had been designed for this transmission line is a braced channel structure (Fig. 2). The cross arms have been placed zig-zag and the conductors are carried on suspension insulators. All these innovations have been introduced to make the line give hazard-free service. The steel earth wire is carried on top where it will besides giving adequate protection against direct strokes provide tie between two adjacent structures and also continuity of earth to reduce chances of potential build-ups. It gives screening against dangerous voltages due to low frequency induction on telecommunication circuits running parallel to power line when single line to earth fault occurs.

The copper conductors are not so exposed to fatigue failures due to vibration phenomenon as are the all-aluminium of A.C.S.R.† conductors more so when it is only a short span construction. Nevertheless, if the study of the region or some parts thereof so indicates or warrants, the parallel wire or stock bridge dampers will be employed. It may be mentioned here that steady winds blowing over long periods in a year cause longitudinal vibrations inthe conductors which result in fatigue failures through reversing stresses of fairly large amplitudes at the nodal points.

There is no provision made for the broken wire conditions in this design. RCT†† structure is also not meant for either angle or dead-end locations (Table 1A).

†Aluminium Core Steel Reinforced.

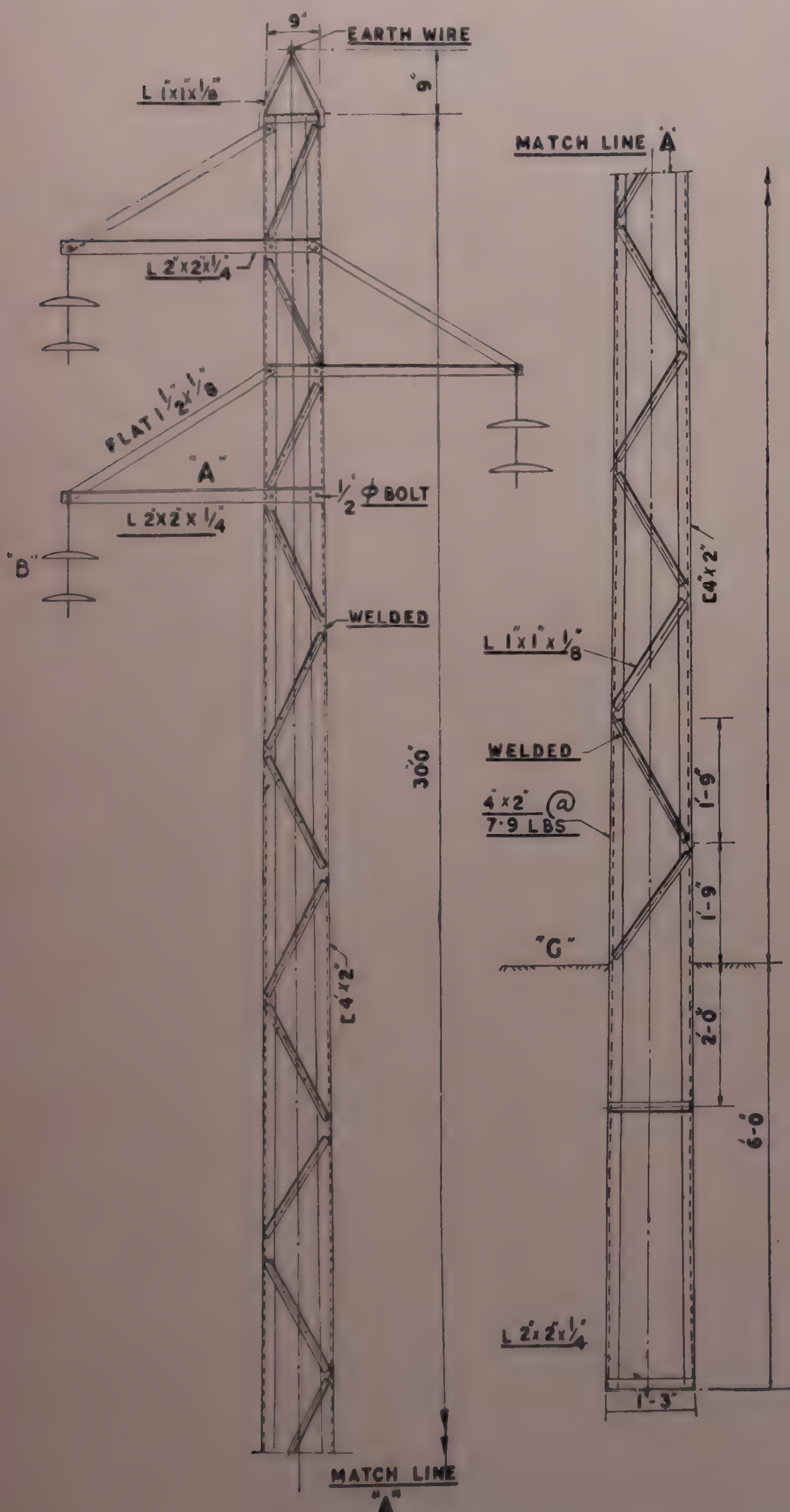
††RCT—after the name of the author.

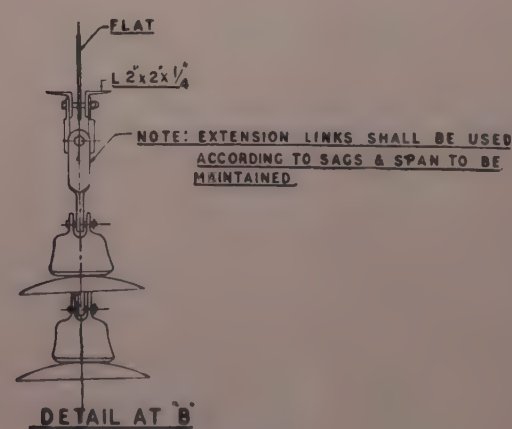
Adequate concreted stay sets will need to be provided at such points. Its fabrication could either be welded or bolted; the former is given preference for as a welded structure it will not be either unwieldy to transport or to erect. Welded joints are more rigid and efficient than the bolted joints and there is not much difference in the cost. Several such poles have been erected with bolted construction; but those have been giving trouble during field erection due to bolt holes either being out or not drilled or punched properly.

The structure is built up with two channels of adequate strength braced with angles (Table 1B). Due consideration has been given that the strength in the longitudinal direction is not less than one quarter the strength in the transverse direction as provided under the Indian Electricity Rules.

To draw an outline diagram of a (attice or a tower structure, one has to take into account all the design loadings including maximum overturning moment to arrive at the base. The base width could be calculated either from fundamental principles or through the empirical formulae, but the final choice of both the base width and the top hamper would invariably be a compromise between the calculated figures and those arrived at through field experience. The bracings have been also staggered in the two faces to give an additional strength to the structure.

The prototype tests were conducted and the structure withstood the designed loadings with a required factor of safety. This structure could be used both for heavy single circuit 33 or 11 kV lines. It is meant for 800 lbs working load. Under no circumstances it shall be used for lighter construction otherwise the design would be uneconomical. The tie member of the bottom cross-arm may be provided with insulating sleeve and given a coat





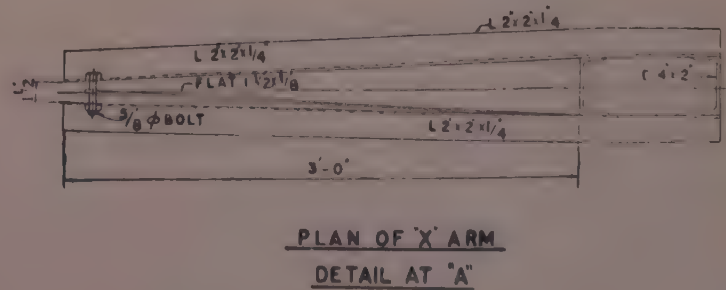


Fig. 2—RCT structure of 11 and 33 kV line with suspension strings.

TABLE 1B—Calculations for the design of RCT Structure

Design for Channel Iron Legs

Assumed span = 400 ft.

Wt/1000 yds. of copper conductor 7/.136=1186 lbs.

$$Wt/ft.=W=\frac{1.186}{3}=0.395 \text{ lb.}$$

Wt of conductor per span=.395×400=158 lbs.

Wt. of 3 conductors=158×3=474 lbs.

Wt. of earth wire/span

(where 3520 yds.=570 kgms.)=48 lb.

Total vertical loading=474+48=522 lbs.

$$\text{Vertical loading on one channel (WV)} = \frac{522}{2}=261 \text{ lb.}$$

Eccentric loading WE

$$\frac{3\frac{10}{12}(158+250)}{\frac{13.68}{12}}=\frac{408\times 3\frac{10'}{12}}{\frac{13.68}{12}}=WE$$

(*a*) Where 250 lb. is the weight of the man with tools.

(*b*) Where 10″ is the width of the pole at the bottom of the lowest cross-arm and 13.68″ is the width of the pole at the section of a-17.

$$WE=\frac{408\times 23\times 12}{6\times 13.68}$$

$$=\frac{816\times 23}{13.68}=1370 \text{ lbs.}$$

So total load on a-17 =18464+261+1370
=20095 lbs.

Now let us take a channel iron section of 4″×2″

$$F=37400-162\frac{L}{R}\text{ lb./sq. inch}$$

where $\frac{L}{R}$ should not exceed 150

R=Radius of Gyration of Channel iron 4″×2″
=0.6″.

Unsupported length (L) should not exceed =150×0.6
×90″

L in our case is 1.87×2=3.74′=44.88″

Say 45″.

$$\text{Therefore } F=37400-162\times\frac{45}{0.6}\text{ lb./sq. in.}$$

=37400−12130 lb./sq. in.
=25270 lb./sq. in.

Therefore yield point load for 4″×2″ section

Channel iron =F×area
=25270×2.341 lbs.
=59,000 lbs.

Factory of safety =2.5

Actual working load
(maximum in a-17) =18464+261+1370
=20,095 lb.

Maxm. working load including factor of safety
=20,095×2.5
=50,237 lb.

Therefore, channel iron section
4″×2″ wt. 7.91 lb./ft. is quite safe.

TABLE 2—Calculation for the Design of the Bracings

Maxm. stress will be in the bracing C3

C3 as measured from the stress diagram
=1920 lb.

The bracing will share half the load because of two faces.

$$=\frac{C3}{2}=\frac{1920}{2}$$

=960 lbs.

Now let us take an angle iron section of
1″×1″×1/8″ (25×25×3)

$$F=37400-162\frac{L}{R}\text{ lb./sq. in.}$$

where $\frac{L}{R}$ should not exceed 200

L=length of the bracing=0.94″ as per drawing where 1″=2 ft.

=2×94=1.88 ft.

=22.56 in.

=22.56×2.54 cm.

=57.2 cm.

R=0.47 cm. i.e. $\frac{L}{R}\angle 200$

$$\text{Therefore } F=37400-162\times\frac{57.2}{0.47}$$

or F =37400−19700
=17700 lb./sq. in.

Therefore yield point load for 25×25×3 M

Angle iron

$=17700\times\frac{1.41}{2.54\times 2.54}$ where 1.41 is the sectional area of the requisite angle in cm^2

=3870 lbs.

Taking a factor of safety of 2.5

Max. load including factor of safety=960×2.5=2400 lbs.

Therefore angle iron section 1″×1″×1/8″ (25×25×3) MM is quite safe.

TABLE 3—Stresses as Measured & Calculated from the Stress Diagram

a 3	1.1″	=	1760 lb.	
a 5	3.13″	=	5008 ,,	
a 7	4.9″	=	7840 ,,	Scale 1/2″=800 lbs.
a 9	6.6″	=	10560 ,,	
a11	8.0″	=	12800 ,,	
a13	9.28″	=	14848 ,,	
a15	10.48″	=	16768 ,,	
a17	11.54″	=	18464 ,,	

So, maxm. stress in the leg member is in a-17, and
,, ,, in the Bracing member is in c.3

TABLE 4—CALCULATION FOR THE DESIGN OF THE CROSS ARM

W 1 = 158 lbs. (Wt. of conductor)
+ 250 lbs (Man with tools)
= 408 lbs.

So vertical load on each of the two sections of the cross arm =204 lbs.

Total windage $W2=\frac{0.408\times 15\times 400}{12}=204$ lbs.

W2 on each section=102 lbs.

Stress due to vertical loading in the angle iron section

$\frac{W1}{2}\times\tan\theta=\frac{204}{21}\times 36=350$ lbs.

So total load in section S or S2=102+350 lbs. =452 lbs.

Now let us take an angle iron section of $2''\times 2''\times\frac{1}{4}''$ i.e. (50×50×6) MM

$F=37400-162\frac{(L)}{R}$ lb./sq. inch where $\frac{L}{R}$ is not to exceed 150.

$=37400-162\frac{(37.5\times 2.54)}{.96}$ lb./sq. in.

where 0.96 is the radius of gyration of the above angle iron section in CMS.

=37400−16050 lb./sq. in.

=21350 lb./sq. in.

Therefore total permissible load for 50×50×6 MM angle iron

=F×area.

$=\frac{21350\times 5.68\ CM^2}{2.54\times 2.54}$ lbs.

=18800 lbs.

Taking a factor of safety of 2.5

maxm. working load including factor of safety=

=452×2.5=1130 lbs.

So the section is very safe.

Note: $2''\times 2''\times\frac{1}{4}''$ section is being used for the cross arms from stiffness point of view to bear slipping of conductors in the event of their snapping and also to cater for central concentration of dead loads during erection or maintenance.

of araldite to eliminate chances of outages through birds perching on top conductor near the insulator string and causing flashover with the tie member.

The $\frac{L}{R}$ or the slenderness ratio has not been allowed to exceed 150 for leg members and 200 for bracing members. The compression formula which is used for this design had been pretested through analytical studies conducted in the design field for its economy and efficiency and the prototype test carried out on the structure has also ratified to that effect.

The leg (Table 1B) and the bracing members (Table 2) have been designed on the basis of their respective maximum stresses as obtaied from the stress diagram (Fig. 1, Table 3). The cross-arm (Table 4) has been designed for dead loads and the stress due to windage. A margin has also been left to bear jerks through slipping of conductor in the event of its snapping.

Conclusion

It would precisely be wrong and unwise to haphazardly design or construct transmission and distribution lines. It should be ensured that the poles or the structures used are adequately safe and conductors and earthwires are so spaced and placed that there is pactically an immunity from all types of line hazards. Sags and tensions should also be given due consideration. Hazard-free transmission lines not only serve well but also save valuable equipment and machinery from severe breakdowns and damage.

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An Automatic Device for the Complete Operation of An Ion-Exchange Column

By

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A simple laboratory apparatus has been devised for automatic operation of an ion-exchange column under desired condition. With this apparatus the performance of any ion-exchange materials can be predicted after running for several hundred cycles within a short time.

The importance of ion-exchange resins, both cationic and anionic, in the various industrial fields has led to the development of such materials having a wide range of properties. The evaluation of these materials is done normally by assessing their ion-exchange capacities, chemical stability towards various conditions of pH and temperature, their attrition characteristics, etc. The suitability of such resins for any commercial application is judged by their performance over a long period under actual conditions of operation. In the normal operation in the plant, regeneration being effected once or twice per day, the long range performance of resin cannot be predicted without running the plant for several years.

It was, therefore, found necessary to develop a method for the complete operation of the ion-exchange process of treatment in the laboratory, which will operate all the cycles of backwash regeneration, rinsing and exhaustion automatically several times a day. The process will, thus, indicate its performance after running for several hundreds of cycles within a short period. Although in the literature[1,2] the use of various apparatuses in some of the laboratories has been mentioned, these are complicated and require elaborate instrumentation, and hence are not applicable to all laboratories.

A simple apparatus has been developed in this laboratory for automatic operation of all the cycles of backwash, regeneration, rinsing and exhaustion under desired conditions. It consists of a float with a vertical stem the movement of which controls a series of valves operating the various sequences of the ion-exchange column. It has several advantages, viz. (i) the time taken for one complete cycle and also for individual operations can be varied easily; (ii) the nature, concentration and flow rates of influents can be changed at will; (iii) the temperature of operation can be varied from room temperature upto 90°C; (iv) the effluents from the resin column during different operations can be collected separately; and (v) it can be constructed using ordinary appliances available in all laboratories.

Details of Apparatus

The apparatus (Fig. 1) consists of a metallic or glass cylinder (L) with two openings at the bottom, one of which is used for supplying the water through a constant head device (O) and another connected to a siphon arrangement. A float (K) is made of a short-necked round-bottom flask of either glass or metal, with a long vertical stem attached to it. The guide (Q) helps the vertical movement of the stem. The hinges (G and H) are attached to the stem with the help of a clamp (T), and their positions can be changed by adjusting the clamp. The details of hinges are given in the inset (Fig. 1). One of the hinges (G) is held in such a position that it can move upwards only to 90°C but not downwards, while the other (H) can move only downwards. The hinge (G) controls the operation of backwash and

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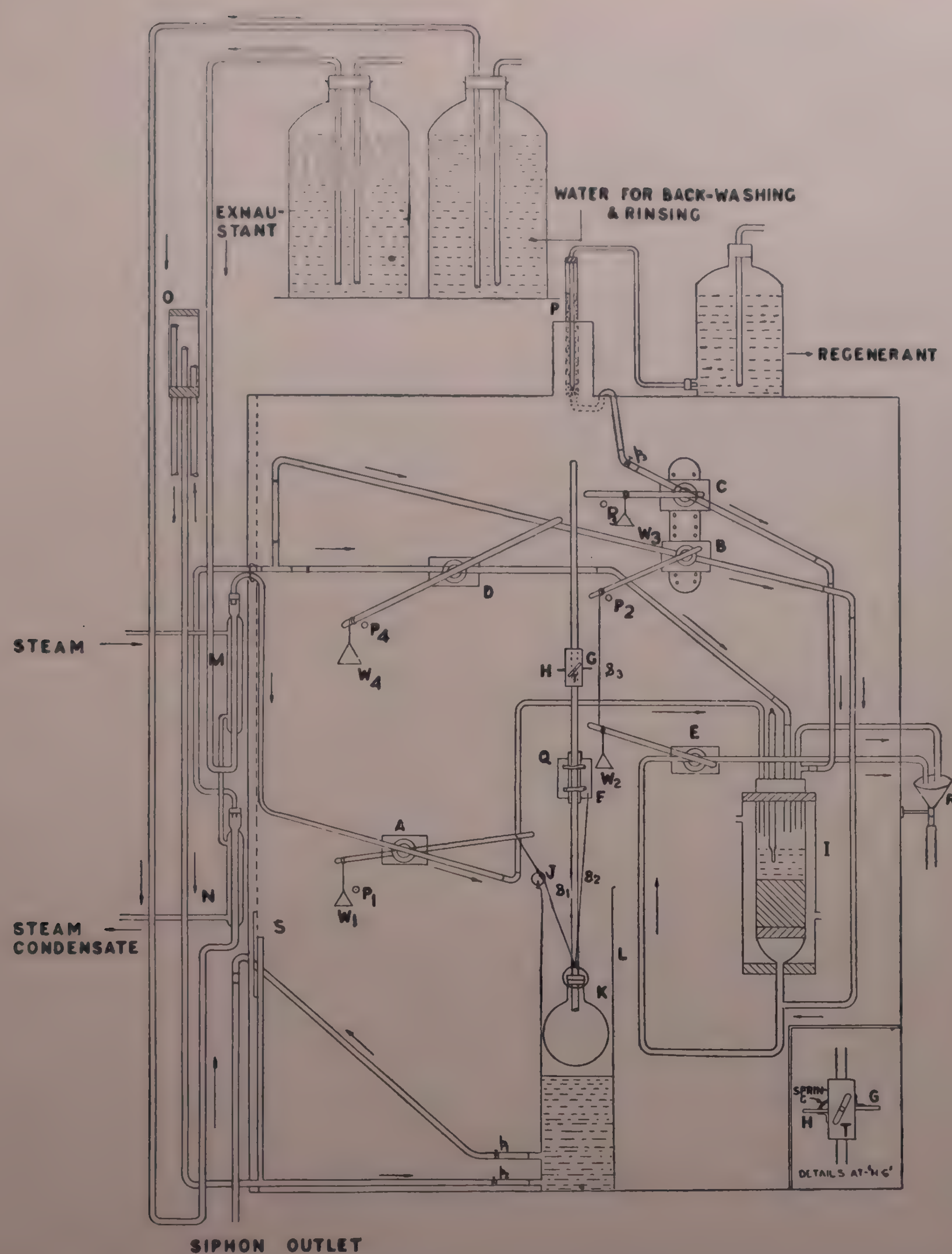

Fig. 1—Apparatus for continuous automatic operations of Backwash, Regeneration, Rinsing, and Exhaustion of Ion-exchangers.

Legend

A. Control Valve for Exhaustant
B. Control Valve for Backwash
C. Control Valve for Regenerant
D. Control Valve for Rinsing
E. Control Valve for Effluent
F. Pin for Tightening the Thread to Support the Float
G. Hinge which can move Upwards but not Downwards
H. Hinge which can move Downwards but not Upwards
I. Ion-Exchange Resin Column with a Jacket
J. Pulley
K. Float
L. Metallic or Glass Cylinder of Suitable Diameter in which Float can Move Freely
M. Heat Exchangers Required to Raise the Temperature of Exhaustant.
N. Heat Exchangers for Raising the Temperature of Liquid for Backwash and Rinsing
O. Constant Head Device
P. Glass Column for Putting Regenerant in the Column
Q. Guide for Keeping Stem in Vertical Position
R. Receptacle
S. Slot for Adjusting Siphon Outlet
T. Clamp for Holding Hinges in Position

P_1, P_2, P_3 and P_4—Pins Supporting Different Levers.
W_1, W_2, W_3 and W_4—Weights Acting on Levers to Bring them back in Normal Position.
S_1, S_2 and s_3—Strings.
P_1, P_2 and P_3—Pinch Cocks.

regeneration, while the other hinge (H) controls the rinsing operation. The flow of the exhaustant is controlled by a simple string (s_1) attached to the float and lever connected to the stopcock (A).

The different stopcocks (A, B, C, D and E), the glass columns (I and P) for the ion-exchange resin and for putting the regenerant into the resin column respectively and the heat exchangers (M and N) are arranged over a wooden framework, and held in position by clamps. The levers are connected to stopcocks in order to facilitate their operation. The levers are counter-poised with suitable weights, and the movement is restricted by fixing pins at suitable positions on the frame.

The extent of downward movement of the float (K) is adjusted by the length of the string (s_2) tied from a point (F) on the frame to the float and the time and flow of the exhaustant can be adjusted by this length. A pulley (J) is mounted at the edge of metallic cylinder for easy movement of the string connecting the lever attached with the stopcock (A) and the float (K).

The glass column for the ion-exchange resin (I) is provided with a jacket and is clamped to the frame with all the connections for backwashing, regeneration, rinsing and exhaustion lines. For operation at higher temperature, one heat exchanger (M) is fitted on the side of the board for heating the exhaustant, while the other (N) is for heating the water for backwash and rinsing. A constant head device (O) has been made for giving a constant flow of water in the metallic cylinder, and three reservoirs are kept on the top containing the liquids required for exhaustion, backwash and rinsing, and regeneration.

Working of Apparatus

The flow of water from the constant head device (O) to the cylinder (L) having the float (K) is so maintained that the siphoning rate of the water from the cylinder is always more than the inlet rate. These rates are being adjusted by the pinch cocks (p_1 and p_2) provided in each line. With the rise of water level the float rises and the strings (s_1 and s_2) attached to the float are loosened, so the stopcock (A) gradually closes due to the cylinder, the counter-weight (W_1) is attached to it by a lever. The movement of the lever is arrested by a pin (P_1) fixed on the board at a suitable distance below the stopcock (A); at this position, the stopcock (A) is closed completely and the flow of the exhaustant to the resin column stops.

With further rise of water level in the cylinder, the float along with the vertical stem rises. As the hinge (G) also rises, it opens the stopcock (B) thereby allowing the water for backwashing to flow through the resin column. The opening of the stopcock (B) also closes the other outlet stopcock (E) of the ion-exchange column. After the further upward movement of the hinge (G), the lever attached to stopcock (B) slips down and is closed again due to the counter-weight (W_2), thereby opening again the stopcock (E).

With further rise of water level in the cylinder, the hinge (G) operates the lever attached to stopcock (C), gradually opening it to allow the regenerant to flow through the resin bed. As the float rises further, the siphoning outlet starts working at a predetermined point and the float gradually starts coming down with the water level in the cylinder. As the hinge starts coming down with the commissioning of the siphon, the lever attached to stopcock (C) also moves down due to the weight (W_3) attached at its end till it attains the normal position, i.e. closed position.

During the downward motion of the float, the other hinge (H) pulls down the lever attached to stopcock (D), gradually opening it, through which the water for rinsing the resin bed enters into the column (I). At a fixed point, the contact between the hinge and the lever is broken causing the return of the stopcock (D) to its normal position, due to the counter-weight (W_4).

As the float starts coming down further, the strings (s_1 & s_2) attached to the float get stretched and open gradually the stopcock (A), through which the liquid for exhaustion starts flowing into the resin bed. On reaching to its original position, the stopcock (A) is opened for a constant flow of the exhaustant. The water level in the cylinder continues to fall till the siphon outlet point is reached. The time of the exhaustion liquid required to pass through the column could be regulated by adjusting the gap between the float and the siphon outlet. On completion of the siphoning operation, the water level in the cylinder starts rising because the water from the constant head device (O) continues to flow. After some time the water level again touches the float and gradually rises along with the rise of water level in the cylinder. Thus, one complete cycle is carried out automatically for different operations. The effluent flows through the stopcock (E) and the funnel (R) to the collection vessel or drain.

The total time taken by each cycle can be varied by adjusting the inlet and the outlet water in the cylinder. The time taken for the rinsing and the backwashing operations relative to the total time can be varied by adjusting the length of the levers on the stopcocks (D and B) respectively, so as to increase or decrease

the contact time between the hinge and the levers. The time taken for exhaustion can be adjusted independently by changing the position of the siphon outlet of the cylinder or by varying the length of strings (s_1 & s_2) attached to the float (K). The time of flow of the regenerant through the column can be varied by adjusting the height of siphon outlet tube in the slot (S) on the side of board. The rate or volume of regenerant in every regeneration can be varied by the pinch cock (p_3) provided in the line.

Thus, once adjusted for all operations of backwash regeneration, rinsing and exhaustion, the apparatus becomes completely automatic and can work for any number of operations desired. The apparatus has proved extremely useful in the study of ion-exchange resins, particularly for determining the stability and capacity changes after running for a large number of cycles, equivalent to few years operation in a normal commerical plant.

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Corrosion by Steam Condensate: Two Case Histories

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Corrosion by steam condensate of cupro-nickel and brass secondary ejector tubes in a power plant and of mild steel evaporator tubes in an ammonium sulphate-nitrate plant has been observed. The reasons for the failure have been investigated.

Condensates are normally supposed to be non-corrosive, but at times they become corrosive due to bacterial action and/or pollution from other sources[1,2,3]. One such case happened at the power generation plant at Sindri due to pollution of feed water with the factory effluents. Another similar problem was encountered in the air conditioning unit of the ammonium sulphate-nitrate plant, where the condensate was contaminated with salt from the ammonium sulphate evaporators. Studies on these two cases of corrosion are described in this paper.

Experimental

Weight-Loss Experiments: Weight-loss experiments were carried out by using mild steel rectangular test coupons of $6 \times 2.5 \times 0.3$ cm size*. For surface preparation and degreasing the procedure described in a previous communication[4] was followed. The coupons were kept immersed for 24 hours in the respective solutions by hanging with a glass hook passing through a hole drilled in the test coupons. The experiments were performed in partially filled stoppered conical flasks. At the end of 24 hours, the coupons were taken out, washed, treated with inhibited hydrochloric acid, degreased and weighed; the loss in weight was recorded as mg./sq. dm/day.

Metallographic Examination: Samples were cut out from the affected and unaffected portions. They were

*Manufactured by Tata Iron & Steel Co Ltd. Jamshedpur (Specification IRSM-16/49)

polished, etched nad examined under a microscope.

For analysis of the condensate samples, the standard procedures[5,6] were followed. All the chemicals used were of the A. R. grade.

Corrosion in Power Generation Plant

Severe corrosion of secondary ejector tubes occurred resulting in leakages and consequent tube replacements involving regular shut-downs. The material of construction was cupro-nickel (specification BSS 257 CN 107); subsequently brass tubes were being used as replacement for the failed cupro-nickel tubes. The cooling water (turbo-condensate) passed on the tube side at 128°-130°C, while the steam passed on the shell side. The primary ejector tubes work under vacuum, while the secondary ones at 2 lbs./sq. in pressure.

An examination showed deep etching marks with gradual thinning of the tubes on the steam side. Metallorgraphic examination of the failed cupro-nickel and brass tubes did not show cracks, fissures, pits or any other similar defect. A detailed chemical analysis of the boiler feed water and ejector condensate from the secondary ejector tubes were made over long periods; some of the data are given in Table 1. It will be observed from the results that the ejector condensate contained appreciable quantities of dissolved ammoniacal nitrogen, nitrate and nitrite nitrogen, carbonate and chloride. Since the pH values were in the range of 4.5 to 5.1, the failure of the tubes might be ascribed to the corrosive action of these ammonium salts; due to its nickel content the cupro-nickel tubes showed greater resistance to the action of condensate than the brass tubes. The failure therefore, can be ascribed to the progressive thinning of the metal due to the dissolved ammonium salts. The dissolved impurities in the condensate had come from the steam issuing from the boiler, since no other possible source of contamination could be traced. It was found that the boiler feed water was contaminated with high concentration of ammonium salts. It was also observed that the entire quantity of water required for the power plant was taken from the river *Damodar* at a point where the factory effluents, containing ammoniacal liquor and other waste products including biological oxidation products, joined the river. To overcome the trouble, the intake of feed water was shifted to a point upstream in the river, and immediately the quantities of contaminants decreased to a low value in the boiler feed water as well as in the ejector condensate (Table 1). Thereafter, the frequency of ejector tube failure has very greatly decreased.

Corrosion in an Air Conditioning Unit

In this case severe pitting and corrosion of the mild steel evaporator tubes occurred, and at one stage the tubes failed at the rate of one per day. The air conditioning unit employs the ammonia cooling system. In the evaporator tubes, ammonia flows through the shell side and the condensate through the tube side. An examination of the tubes showed pitting and consequent perforations from the condensate side. The condensate, which circulated through the tubes, was taken from the steam issuing from the ammonium sulphate evaporators. The circulation rate of the condensate was 36 m^3/hr. and the average temperature ranged from 0-20°C. A typical analysis of the fresh condensate collected from the ammonium sulphate evaporators and that circulat-

TABLE 1—ANALYSIS OF EJECTOR CONDENSATE AND BOILER FEED WATER

(Only max. and min. values obtained over long periods are given.)

Sl. No.	Sample	Ammoniacal N, ppm	Nitrite+ Nitrate N, ppm	CO_2, ppm	Cl, ppm	T.D.S., ppm	T.S.S., ppm	pH	Remarks
1.	Ejector condensate	36.7 - 488.4	1.3 - 6.4	14.8 - 34.4	9.1 - 12.3	30.0 - 78.0	10.0 - 20.0	4.6 - 5.1	In both these cases the feedwater to the plant was contaminated with factory effluents.
2.	Boiler feed water	5.8 - 17.7	0.7 - 1.4	—	—	—	—	10.1	
3.	Ejector condensate	0.5 - 0.8	0.1 - 0.5	—	4.4 - 7.4	—	—	4.6 - 5.4	In both these cases the feed water to the plant was not contaminated with factory effluents.
4.	Boiler feed water	1.0 - 1.9	0.4 - 1.2	—	2.9 - 4.0	—	—	9.7	

ing through the tubes is given in Table 2. The results show that the dissolved salt in the fresh condensate is ammonium sulphate, while the condensate circulating through the evaporator tubes contained, besides ammonium sulphate, some free ammonia probably due to leakages in the tubes. Corrosion tests with mild steel coupons (Table 3) showed that the corrosion rate varied between 22 to 34 mg./sq. dm./day with severe etching and pitting of the coupons; hence, although the weight losses were small the quick failure of the tubes might be ascribed to localized pitting.

Sodium dichromate was tried as an inhibitor. Table 3 shows the effect of increasing concentration of dichromate. At a CrO_4 concentration of 1000 ppm, the corrosion and pitting tendencies were completely eliminated. The remedy would, therefore, be to maintain a residual of 1000 ppm CrO_4 in the initial stage at a pH of 7.0 to 7.5. The chromate residual might be subsequently reduced to a lower value, based upon studies in the plant.

TABLE 2—ANALYSIS OF CONDENSATE SAMPLE FROM AMMONIUM SULPHATE-NITRATE PLANT

Sl. No.	Ingredients	Condensate from the Air Conditioning Unit	Fresh Condensate from the Ammonium Sulphate Evaporator
1.	pH	9.5-9.9	8.8
2.	Ammoniacal N, ppm	248.8	7.3
3.	$(SO_4)^{2+}$, ppm	44.5	29.6

None of the samples contained nitrite, nitrate or chloride.

TABLE 3—EFFECT OF CrO_4 ON THE CORROSION OF MILD STEEL IN CONDENSATE FROM AIR CONDITIONING UNIT AND AMMONIUM SULPHATE EVAPORATORS

[Vol. of solution 400 ml. temp., 15°-28°C]
pH 7.0-7.5

Expt No.	Conc. of Dichromate as CrO_4 ppm	Corrosion Rate in Fresh Condensate from Evaporators, mdd.	Corrosion Rate in Condensate from Air Conditioning Unit, mdd.	Remarks
1.	—	22.5	35.7	Severe pitting and etching are observed, more in condensate from air conditioning unit
2.	200	—	10.8	
3.	300	3.0	9.7	
4.	400	No corrosion	1.4	
5.	500	,,	1.4	
6.	600	,,	1.3	
7.	800	,,	1.3	Coupons Bright and shining
8.	1000	,,	No corrosion	
9.	1500	,,	,,	

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The authors wish to thank Dr. K. R. Chakravorty, General Manager, for his interest in this work.

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On Synthetic Zeolites

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The synthesis of some zeolites with sodium as cation has been reported. The activity of the samples towards water vapour has been determined and compared with that of an imported 5Å molecular sieve.

The crystalline alumino-silicates of alkali and alkaline-earth metals, like sodium, potassium, calcium, etc., having channels of strictly definite dimensions, which allow the molecules of smaller sizes to pass through excluding the molecules of larger sizes, are now-a-days largely synthesized in the laboratory[1–6]. The pores made of oxygen atoms regulate the adsorption of the molecules, and there may be more than one kind of such pores in the same molecular sieve. It has been shown[7–8] that LMSA* has windows of dimensions 4.2 (8-membered 0-ring) and 2.2 Å (6-membered 0-ring) along with a central cavity of diameter 11.8Å (α-cage) and smaller cavity 6.6Å (β-cage). Each unit cell of LMSA contains $12AlO_4$ and 12 SiO_4 tetrahedra and 12 monovalent cations. Eight cations occupy central sites of a 6-membered-ring. When a zeolite is dehydrated, the cations locate themselves on the walls of the cavity. They have a pronounced effect in determining the pore diameter[9–10].

Attempts have been made to synthesize zeolite in this laboratory as it is not produced in India. The constituents used are sodium silicate, sodium aluminate, and caustic soda. A silicate solution (approx. 20 g./l.) is mixed with aluminate solution (16.7 g./l.) so that the ratio of SiO_2:Al_2O_3 is maintained at 2:1–3, followed by the addition of enough caustic soda in order to make the solution nearly 3M with respect to caustic soda. The gels formed are crystallized by the hydrothermal technique in autoclaves made of Pyrex glass. The three samples reported here are crystallized at 114 (3H), 120 (4H) and 95°C (8H), the crystals having[12–13] the following compositions: 3H (SiO_2 49.99, Al_2O_3 22.95 and Na_2O 8.9%), 4H (SiO_2 39.8, Al_2O_3 27.1 and Na_2O, 5.7%), 8H (SiO_2 39.9, Al_2O_3 31.55, and Na_2O 18.32%). The specific gravities and refractive indices of the samples are 2.03 (3H) 2.08 (4H) and 2.18 (8H) and 1.50 (3H), 1.51 (4H), 1.48 (8H) respectively.

To the samples 3H and 4H, 10 per cent kaolin was added, while 8H did not contain any kaolin. All the samples were activated by heating in air at 450°C for 6 hours.

X-ray studies showed a general agreement of the structures with the zeolite systems (Fig. 1). The samples

*Linde Molecular Sieve, Å

3H
5A
8H
4H

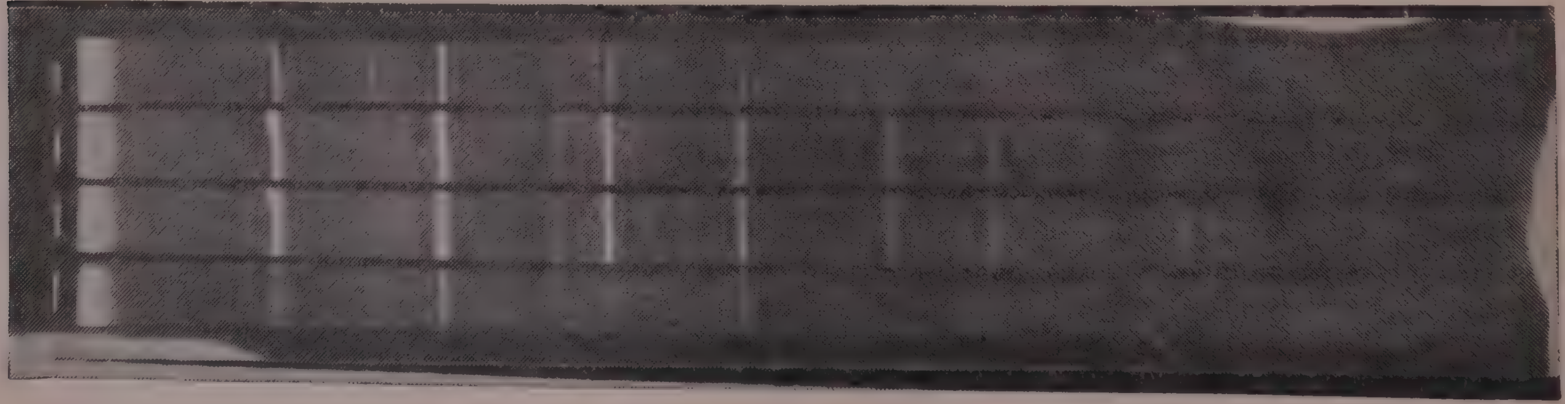

Fig. 1—X-ray photographs of different zeolites.

8H and 5A (E. Merck) were identical. The samples 3H and 4H did not belong to the same zeolite system as 8H. The activity with respect to the water was determined at $P/P_s=0.8$; the values were 18.75 (3H), 10.9 (4H) and 9.5 per cent (8H). The imported item (5A) had an adsorption capacity of 22.86 per cent at $P/P_s=0.8$. The rather low value of water adsorption should be viewed in the light of the observation made by Zhdanov[14] for certain zeolites prepared in his laboratory.

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Notes & News

Production of Granular Ammonium Sulphate Using the TVA Ammoniator-Granulator

A process for producing well-shaped, hard granular ammonium sulphate has been developed by the Tennessy Valley Authority. In this process sulphuric acid (93%) was partially ammoniated in a preneutralizer to an $NH_3 : H_2SO_4$ mole ratio of about 1: 1 and the ammoniation was completed in the ammoniator-granulator where the product was granulated simultaneously. An $NH_3 : H_2SO_4$ mole ratio of 1: 1 was used in the preneutralizer to take advantage of a high point of solubility for the system $NH_3.H_2SO_4.H_2O$. By controlling the temperature of the boiling liquid at about 310°F through addition of water, a clear solution containing only 10% water and having a low viscosity was obtained.

The solution from the preneutralizer was fed to the ammoniator-granulator where the remainder of the required ammonia was introduced beneath the rolling bed of solids. Granulation was controlled by the rate of addition of undersize material and crusted oversize material. A recycle ratio of 2.5 pounds per pound of product was satisfactory. The granular product contained only 0.1% moisture and required only cooling before screening. The preneutralizer to be constructed has to be lined with acid resistant brick for checking corrosion.

[*Nitrogen*, No. 45 (1967), 33]

Potassium Schoenite as Fertilizer

CSMCRI Bhavnagar has developed a process for the manufacture of potassium schoenite—a double sulphate of potassium and magnesium with six molecules of water of crystallization and with K_2O and MgO contents as 22-24 and 8-10 per cent. Field fertilizer trials conducted by the above institute on *bhindi*, groundnut and tobacco have indicated that for the first year potassium schoenite gives higher yields than potassium chloride or sulphate.

Cost estimates for different capacity potassium schoenite plants ranging from 1.5 to 10 tonnes per day have shown that a plant of the smallest capacity (1.5 tonnes) is economical. Thus, even salt works of 15000 tonnes capacity which can produce enough mixed salt for 1.5 tonnes can produce potassium schoenite economically.

Roy L. Donahue and H. Sankarasubramoney of Ford Foundation Intensive Agricultural District Programme, New Delhi have opined that potassium schoenite should be an ideal fertilizer for crops of the western coast of India. Potassium and magnesium deficiencies have been noticed widely in most of the soils on that coast. The soils are porous and highly leached due to heavy rainfall. This region comprises of all the districts in Kerala, west coasts of Mysore and Maharashtra and the Nilgiri of Madras. The current average fertilizer recommendations for crops in this region are given below:

Crop	Approximate Area, '000 acres	Current Average Fertilizer Recommendation $N+P_2O_5+K_2O$, lb./acre
Coconut	1600	35+35+70
Arecanut	250	50+25+100
Rubber	377	30+50+50
Coffee	281	40+60+60
Tea	185	60+30+30

[*Salt Research & Indus.*, **4** (1967), 32, 28 & 35]

Fertilizer or Famine

In considering the food problem, the world is to be viewed in terms of two regions—the developed and the developing—the former comprising of N. America, W. & E. Europe and Oceania (Australia & N. Zealand). The developing world comprises Asia (excluding Japan), Africa and Latin America, While total grain production increased in both regions, per capita grain production increased only in the developed country, the four-fifths of the grains in the developing region are due to expansion of cultivated area and only one-fifth due to increase in yield per hectare. The per capita output of food in the developing world has steadily declined in the last few years. During the years preceding World War II the developing regions of Asia, Africa and Latin America were all net exporters of grain, but after the war the flow was reversed.

The import of foodgrains in India was 3.5 m. tonnes in 1961; the same has increased to 6.37 and 15.0 millions in 1964 and 1965. Two-thirds of the increase in production during past 15 years have come from increase in area and one-third in per hectare yield. There is not much scope in future for increasing the area further in India because in that case farming will become more dependent on the vagaries of nature and require higher outlays in capital in land preparation and clearing, irrigation and drainage, etc. So the increase in food production has to come through an increase in yield per hectare (in Japan per hectare yield of rice is four times that of India).

The most important single factor in increasing the yield per hectare is fertilizer, which accounts for about 50 per cent increase in agricultural production in U.S.A. since World War II. According to the best conservative estimates, a tonne of plant nutrient (N, P_2O_5 and K_2O) will produce 10 tonnes of foodgrains, and assuming that one tonne foodgrain can support 5 persons a year at the rate of about 500g./head/day after aollowing for seed, wastage etc. one tonne of plant food will feed 50 persons for one year. The annual rate of increase of population is 12 million, so to feed them annually an additional 240,000 tonnes of plant nutrient will have to be produced or imported. In the new fertilizer factories the cost of production of one tonne of plant nutrient is expected not to exceed Rs. 1,500. Therefore the cost of feeding a person through fertilizer works out to be about Rs. 30. Union Minister for Irrigation has said that to meet the challenge of the increase of population, India has to bring an additional 2 million acres under irrigation

every year which works out to Rs. 100 for irrigation for every person born. It will thus be evident that the cost of feeding a person through fertilizer is much less than through irrigation.

More attention has been paid in this country to provide irrigation than supply of plant food. As a result, India has the highest percentage of land under irrigation and one of the lowest per hecare and per capita consumption of fertilizer in the world (Table 1).

TABLE 1—PERCENTAGE OF IRRIGATED LAND AND PER HECTARE AND PER CAPITA CONSUMPTION OF FERTILIZER.

	Percentage of Irrigated Land	Fertilizer ($N+P_2O_5+K_2O$) consumption, kg/hectare	Fertilizer ($N+P_2O_5+K_2O$) consumption kg/capita
USA	7	51.59	50.45
Japan	8	279.68	10.81
India	16	3.68	1.29

No doubt India ranks second in world population but its population is not densest per hectare of cultivated land. Japan has 15.2 persons, Belgium 9.2, Italy 3.2 and India 3.2 per hectare. It can, therefore, be said that the land in India is not over-populated but under fertilized.

[Fertilizer News, **12** (6) (1967), 18]

Syngas Purifier Cuts Ammonia Costs

C. F. Braun and Co. has developed a new purifier process to be used in large ammonia plants. The key process features are mild reforming conditions and the ability to economically produce a higher purity synthesis gas for use in the low pressure loop. The consumption of raw materials and utilities is reduced some 10 per cent compared to conventional plants with no increase in capital investment. The first plant to use this process, a 750 ton per day unit, is now on stream for Collier Carbon and Chemical Corp. at Brea, California. The purifier process departs from conventional processing in that (1) more than the stoichiometric amount of air is reacted in the secondary reformer, (2) the excess nitrogen together with methane and argon are removed in a cryogenic purifier producing a high purity synthesis gas. This gas is almost completely utilized in a simplified ammonia synthesis loop with greatly reduced purge requirements. Other features of the process are a simple gas expander to provide the entire cryogenic refrigeration requirement and a gas turbine-driven process air compressor. The gas turbine exhaust provides preheated combustion air for the primary reformer.

The use of excess air in the secondary reformer reduces the fuel reqirement in the primary reformer by one-third. More efficient fuel utilization is achieved by recovering energy from the gas turbine exhaust in the primary reformer. High purity synthesis gas allows minimizing of ammonia synthesis loop purge requirements, a lower cost loop utilizing a single high pressure seperator, reduced heat exchange, lower allowable synthesis pressure and refrigeration requirements.

The steps of purifier Ammonia Process are feed desulphurization, primary reforming, secondary reforming with excess air, carbon monoxide shift conversion using high temperature and low temperature shift beds, carbon dioxide removal, methanation, drying, cryogenic purification, compression and synthesis.

The desulphurized feed gas mixed with steam and preheated to about 900 to 1,000°F in the reformer furnace convection section goes to the primary reformer catalyst tubes in the radiant section. The gas and steam react in the presence of nickel catalyst to form a mixture of hydrogen and carbon oxides. With the purifier process the reformer can operate easily at pressures to 800 psi because satisfactory methanol conversion can be obtained with reasonable reformer tube temperatures. Temperature maintained in the conversion is 1,350 to 1,500°F. Process air from compressor, preheated to above 800°F in the reformer furnace convection section is fed to the secondary reformer. The oxygen in the air reacts with the hydrogen and methane to supply heat for further reforming of the methane to hydrogen. The nitrogen remaining in the gas supplies the nitrogen for ammonia synthesis. In the purifier process some 40 to 50 per cent extra air added in the secondary reformer reduces the primary reformer firing by about 30 per cent. In addition much of the heat is absorbed as sensible heat to raise the reactants to a high temperature and reduce the methane leakage to a low level. In the purifier process the methane is removed ahead of the synloop so that methane leakage of 1.0 to 1.5 per cent is easily tolerated. Consequently secondary reformer outlet temperature may be reduced 100 to 200°F below conventional designs.

The purifier process can be operated with less steam requirement. The effluent from the secondary reformer is cooled to 730°F and then it flows to a bed to conventional iron-chromium catalyst where 75 per cent of carbon monoxide reacts with steam to form carbon dioxide and hydrogen. The gas leaving is cooled to 450°F and flows first to a bed of zind oxide and then to a bed of high activity low temperature copper zinc shift catalyst where most of the remaining carbon monoxide is converted to carbon dioxide. The purifier process has also a second bed of conventional iron catalyst. All of the carbon dioxide is removed from the gas using any of the currently available absorption processes. All CO_2 not removed from the product is reconverted to methane in the methanation.

In the methanator, operations are carried out in less severe operating conditions. The gas before flown to cryogenic purifier must be dried of all water and other components which tend to freeze. The purifier consists of a feed-effluent heat exchanger, a gas expander, a vapour-liquid contacting rectifier column and a reflux condenser. The feed-effluent heat exhanger is a compact braged aluminium, plate-fin heat exchanger of the type normally used for cryogenic device. The design provides for cooling the feed gas by simultaneous heat exchange with both the purifier product and the vent gas. The feed is extracted from the exchanger at a temperature well above the dew point and passed through a turboexpander to develop the net cooling. The gas ex-expander is a radial-inflow reaction turbine with variable inlet nozzles to permit control of the power extraction. The rectifier contains vapor-liquid contacting devices such as aluminium rings, sieve trays or bubble cap trays. The reflux condenser consists of a vertical shell-and-tube heat exchanger integrally mounted on the top of the rectifying column. The bottom tube sheet of the exchanger forms the top of the column. Vapuor from the rectifying column flows upward in the tubes and is partially condensed to provide reflux for the rectifier. Liquid from the bottom of the column is vaporized at a reduced pressure in the shell side of the condenser to supply the refrigeration for

the reflux condenser. Reflux flows down the tubes counter-current to the vapour and drops back into the packing.

Feed to the purifier contains 60 to 70 per cent hydrogen, 30 to 40 per cent nitrogen, 2 to 3 per cent methane, about 0.5 per cent argon. The feed is cooled to a temperature in the range of −200 to −250°F in the first heat exchanger section by heat exchange with the two effluent streams. It then passes through the turbo-expander to provide the required cryogenic refrigeration. The feed is further cooled in the second section of the heat exchanger and then enters the rectifier column. The gas leaving the cryogenic purifier is a 3 to 1 hydrogen-nitrogen mixture containing about 0.2 per cent argon and trace of methane.

Syngas from the purifier is compressed to a pressure ranging from 2,000 psi for a 750 t.p.d. unit to 3,000 psi for a 1,500 t.p.d. unit. Recycle gas is added before the last wheel and the combined flow is fed to the synthesis section which consists of a simple loop. Here it is pre-heated, passed through the synthesis converter, cooled, and the ammonia product condensed. The ammonia product is extremely pure. It conatins no water or carbon dioxide and there is no oil because all compressors are centrifugal.

[*Hydrocarbon Proceesing*, **46** (4) (1957), 197)]

Pesticides in India

India's fourth five year plan tentatively envisages the use of plant production measures on 55 million hectares of cultivated land, in contrast to the 16.5 million hectares covered during the third plan period. An estimated 6 to 7 million tons of foodgrains, nearly 10 per cent of the national foodgrains output, is lost each year because various insects, rodents and other pests. An additional ten per cent loss is attributed to plant diseases, weeds and parasites. But the destruction of foodgrains could be significantly minimized.

The production of pesticides has to be stepped up from the present level of about 18,000 tons to the level of 100,000 tons. A rough estimate of a demand-growth pattern for newer types of pesticides in India during the next 5 to 6 years:

Type	Estimated Demand, tons	Production in 1965, tons
B.H.C.	50,000	7,500
Lindene	1,500	
D.D.T.	8,000	2,800
Endrin	3,000	
Carbaryl	6,000	
Chlordane		
Heptachlor, Aldrin, Dieldrin, Parathion, Demeton	1,000	
Malathion, Phorate, Di Melthoate etc	21,000	240
Copper Oxycloride	6,000	1,300
Thiocarbonates	6,000	60
2, 4-D; 2, 4, 5-T etc.	3,000	60
Ethylene Dichloride	9,000	20
Calcium Cyanide	1,500	
Zinc Phosphate	2,500	250

[N. R. Srinivasan, Agri. Chemicals, **22** (3) (1967), 34]

SNAM Urea Process Uses NH_3 to Strip Carbamate

SNAM-progetti has made a modification in the synthesis of urea from ammonia and carbon dioxide, and the process has been successfully applied on a single train 330,000 ton/year urea plant in Italy. The process differs from other processes in using an atmosphere of pure ammonia to decompose the ammonium carbamate formed in the urea synthesis step. When feed-stock carbon dioxide and ammonia (in the molar ratio 1 : 3 to 1 : 5) are reacted under normal operating conditions, about 60 per cent of the carbon dioxide is converted into urea. Most of the rest of the carbon dioxide is converted to ammonium carbamate.

In the modern "total recycle" process the decomposition of carbamate is effected by lowering the pressure. But both ammonia and carbon dioxide which are thus formed have then to be recompressed and this inevitably means a high utility change. Toyo Koatsu modified the total recycle process by using the carbamate to absorb carbon dioxide formed in the shift reaction of the ammonia plant. The resulting mixture of dissolved carbon dioxide, ammonia, carbamate, water and urea is passed to the urea synthesis unit. This is the integrated ammonia urea process.

In the DSM "carbon dioxide stripping" process carbamate is decomposed subjecting it to the atmosphere of carbon dioxide by reducing its partial pressure. The process avoids the problem of pumping highly corrosive carbamate.

Snam-progetti's new method is an extension of this process. It uses an atmosphere of ammonia rather than carbon dioxide to decompose the carbamate.

In the process, feedstock ammonia and carbon dioxide are passed to a reactor operating either at conventional temperatures and pressures (200-250 atm., 180-190°C) or at lower pressure (120-140 atm.). Unreacted carbamate is separated from the ùrea solution and decomposed into ammonia and carbon dioxide in a specially designed vessel. Pressure is maintained at 120-140 atm. and, in a single-stage operation, ammonia is passed into the decomposer while a high-pressure stream of ammonia and carbon dioxide is taken out. Heat from this exothermic decomposition is recovered in a single-stage condenser as low-pressure steam and is utilized in the plant.

Production Costs in £/ton for 330,000 ton/year Prilled Urea Plant

Item	NH_3 stripping	CO_2 stripping	Integrated NH_3	Total recycle
Raw materials	11.5	11.4	11.5	11.5
Utilities	2.2	1.7	1.4	2.5
Labour, maintenance, overheads	0.7	0.8	0.8	0.8
Depreciation and interest	0.9	1.2	1.0	1.2
Total production costs	15.3	15.1	14.7	16.0

If the urea synthesis reactor operates in the higher-pressure range the products from the decomposer must be recycled by means of a pump. On the other hand, if the reactor operates at the same pressure as the decomposer the products from the decomposer can be recycled to the reactor by a gravity feed which avoids the use of pumps.

Part of the unreacted ammonia from the urea synthesis unit is used as a stripping medium in the carbamate decomposer. At 190°C the carbamate decomposition goes almost to completion. The temperature is high enough to minimize the formation of biuret, which can prove an objectionable impurity in the final urea product. The final stages of the urea clean-up and of the prilling operation are quite conventional. Biuret is kept to 0.60 per cent by weight and moisture to 0.25 per cent.

SNAM-Progetti claims four main advantages for this process. First, it claims low utilities consumption and maintenance costs. About 0.4 ton low-pressure steam is produced per ton urea. Second, product quality is high. The prills are pure white and very uniform in size so that a final screening is not necessary. Third, pumping problems are either greatly reduced or (with a low-pressure urea synthesis unit) eliminated. Fourth, the route offers a high degree of flexibility under operating conditions.

Capital costs for erecting plants to battery limits, including engineering know-how and licences, are said to be low. A 100,000 ton/year plant would cost $2.75 m. and a 200,000 ton/year plant $4.00 m.

This goes for both variations in the SNAM process. On the basis of economic data supplied by the Italian concern, total production costs for a 30,000 ton/year prilled urea plant have been calculated and compared these costs with those for the processes. Ammonia has been charged at £ 20/ton and no charge has been made for the carbon dioxide. The table shows that the SNAM-Progetti process offers manufacturing costs fairly close to those of the other recently developed processes. Because capital costs make up only a small proportion of total costs in all the processes, the substantial savings in capital investment claimed for the SNAM-Progetti process do not have a large effect on the total manufacturing costs.

[*ECN*, **11** (273) (1967), 32]

Flexibility in new ammonia plants

For various reasons it is desirable to have flexibility in large ammonia plants which will allow them to operate economically for considerable periods at 50 per cent or less of designed capacity. Of the two kinds of compressors used in ammonia plants to raise the synthesis gas to the required pressure, a reciprocating compressor can cope with up to 120,000 tons/year of ammonia capacity. With very large single train ammonia plants of 200,000 tons/year and above turbine driven compressors are the most economic including the investment cost. But if situations arise, a 200,000 tons/year plant with one of its two reciprocating compressors shut down would show very little increase in operatng costs compared with full capacity working. Whereas a centrifugal compressor plant of the same size would involve heavy energy losses if it were operating at even 60 per cent of capacity. In fact below 60 per cent it is very difficult to get the compressor for a plant of this size to work satisfactorily. The steam make is invariably cut-back *pro rata* with the cut-back in ammonia production which reduces the power supply to the compressor. By its nature, however, the compressor must have a steady load to work against and this has to be supplied by greater recirculation of synthesis gas. In all, the efficiency of a reciprocating compressor declines almost linearly with decreases in operating

COMPARISON OF RECIPROCATING COMPRESSOR WITH CENTRIFUGAL COMPRESSOR IN AMMONIA PLANT PRODUCING 200000 TON/YEAR (600 TON/DAY) AMMONIA

TABLE 1—Two Reciprocating Steam Driven Compressor. Battery Limits Investment $ 12.25 m (£ 4.37 m.)

Percentage of plant capacity employed		100%		70%		40%	
	Unit price	Consumption/ton NH_3	Cost/ton NH_3 $	Consumption/ton NH_3	Cost/ton NH_3 $	Consumption/ton NH_3	Cost/ton NH_3 $
Naphtha:							
for process	$/ton 20	0.535	10.70	0.535	10.70	0.535	10.70
for heating & additional steam generation	$/ton 20	0.280	5.60	0.328	6.56	0.402	8.04
Cooling water	$/m³ 0.0075	210	1.57	216	1.62	290	2.17
Electric power	$/kWh 0.0125	62	0.77	80	1.00	105	1.31
Boiler feedwater	$/m³ 0.20	2.2	0.44	2.3	0.46	2.36	0.47
Chemicals and catalyst			0.75		0.75		0.75
Total variable costs			19.83		21.09		23.44
Operators	$1.75 per hour 6 men/shift		0.42		0.60		1.05
Maintenance	3% per annum		1.84		2.63		4.60
Capital cost	13.5% per annum		8.27		11.80		20.65
Total cost per metric ton NH_3			30.36		36.12		49.74

throughputs, while centrifugal compressor efficiency declines far more sharply. Apart from the higher capital charge associated with reeiprocal compressors, it is also true that shutdowns are very much more a feature of reciprocating compressors.

Friedrich Uhde GmbH's olution to the economics of below capacity working has been to use steam turbine driven reciprocating compressors. One problem which has to be tackled is, of course, the huge gear reduction which is inevitable when a turbine is coupled with a reciprocating compressor. The reduction has to be far greater than with a centrifugal compressor driven by a steam turbine.

Uhde states that the overall heat and steam economy in the total plant is at least as favourable as with a centrifugal compressor plant possibly even a little better on account of the slightly higher efficiency of the reciprocating compressors. The slight increase in initial plant investment can easily be balanced by the fact, that the plant can be regulated down to the desired capacity without any of the energy losses associated with running the centrifugal compressors below maximum capacity. It is significant that a 200,000 ton/year (600 ton/day) plant is the largest so far which uses this system.

TABLE 2—ONE CENTRIFUGAL-TYPE STEAM DRIVEN COMPRESSOR. BATTERY LIMITS INVESTMENT
$ 11.8 m. (£ 4.2 m.)

Percentage of plant capacity employed	Unit price	100%		70%		40%	
		Consumption/ton NH_3	Cost/ton $NH_3$$	Consumption/ton NH_3	Cost/ton $NH_3$$	Consumption/ton NH_3	Cost/ton $NH_3$$
Naphtha:							
for process	$/ton 20	0.535	10.70	0.535	10.70	0.535	10.70
for heating & additional steam generation	$/ton 20	0.291				0.710	14.20
Cooling water	$/m³ 0.0075	230					0.32
Electric power	$/kWh 0.0125	30					0.75
Boiler feedwater	$/m³ 0.20	2.25	0.45	2.37			0.50
Chemicals and catalyst			0.75		0.75		0.75
Total variable costs			19.83		21.99		29.92
Operators	$1.75 per hour 6 men/shift		0.42		0.60		1.05
Maintenance	3% per annum		1.77		2.53		4.43
Capital cost	13.5% per annum		7.97		11.39		19.95
Total cost per metric ton NH_3			29.99		36.91		55.35

[ECN **11** (268) (1967), 36 and **11** (270) (1967) March 31, 26]

Fertilizer from Nuclear Desalination Plants

The production of ammonia with hydrogen generated by the electrolytic decomposition of water requires cheap source of electric power. With power costs of 2.5 to 3.0 mills./kWh currently obtainable on an incremental basis from commercial light water nuclear reactors, and using advanced electrolytic cells that operate at very high current densities, ammonia fertilizer can be produced for an estimated $ 39/ton. If this is compared with the $ 40/ton or more delivered cost of externally produced ammonia, a number of the world's less well developed countries could find the economics of the production of hydrogen and ammonia fertilizer at nuclear desalination plants attractive. Studies carried out in the U.S.A. on the cost of electricity produced in conjunction with desalination have shown that the cost per kWh can be substantially reduced by making the station size very large and power costs as low as 1.6 mills/kWh for large dual purpose desalination reactors producing upto 5,000 MW. The cost of off-peak power from such reactors could be as low as 0.57 to 0.8 mills/kWh.

Table 1 gives comparison of ammonia production costs for the water electrolysis process with the natural gas price in an ammonia reforming plant assuming the use of recent advanced electrolytic cells which operate at current densities up to 1,600 A/ft². The cost of producing ammonia by the electrolytic route using 1.6 mills/kWh power, could therefore be competitive with the cost of using 44 C/10^6 Btu natural gas with no oxygen credit or with 29 C/10^6 Btu natural gas allowing $ 4/ton oxygen credit.

TABLE 1

Examples of Ammonia Production Costs						
Ammonia Plant Capacity, tons NH_3/day	Return on investment %/year	Ammonia via Electrolysis			Ammonia via Reforming	
		Electric power cost mills/kWh	Electrolytic oxygen credit, \$ ton O_2	Ammonia production cost, \$ ton NH_3	Competitive natural gas cost, 10^6 Btu	Ammonia production cost, \$ ton NH_3
3000	4	1.6	0	20.00	41	20.00
3000	4	1.6	2	17.20	33	17.20
3000	4	0.8	2	13.40	21	13.40
300	4	2.5	0	34.80	67	34.80
300	4	2.5	2	32.00	59	32.00
300	4	3.0	0	39.00	80	39.00

TABLE 2—AMMONIA MANUFACTURING COSTS FOR ELECTROLYTIC HYDROGEN AND STEAM-METHANE REFORMING PLANTS—3,000 TONS NH_3/DAY

	15% return on investment				4% return on investment			
	Steam-Methane reforming plant		Electrolytic plant (advanced cell)		Steam-Methane reforming plant		Electrolytic plant (advanced cell)	
Natural gas cost, C 10^6 Btu	20	40	—	—	20	40	—	—
Power cost a.c., mills/kWh	—	—	1.00	1.60	—	—	1.00	1.60
Power cost d.c., mills/kWh	—	—	1.08	1.68	—	—	1.08	1.68
Total capital cost, $\$ \times 10^6$	30.26	30.26	31.27	31.27	30.26	30.26	37.99	37.99
Cell current density (optimum), A/ft^2			1,600				800	
Raw materials and utilities:								
Natural gas	6.60	13.20	—	—	6.60	13.20	—	—
Electric power	—	—	9.72	15.13	—	—	8.82	13.70
Cooling water at 2C/1,000 gal	1.13	1.13	0.95	0.95	1.13	1.13	0.77	0.77
Boiler feedwater at 50C/1,000 gal	0.50	0.50	—	—	0.50	0.50	—	—
Condensate credit at 50C/1,000 gal	−0.12	−0.12	—	—	−0.12	−0.12	—	—
Labour and supervision:								
Operating labour at \$4/man-hour	0.20	0.20	0.27	0.27	0.20	0.20	0.27	0.27
Maintenance labour at \$4/man-hour	0.25	0.25	0.34	0.34	0.25	0.25	0.34	0.34
Operating supervision at \$5/man-hour	0.08	0.08	0.11	0.11	0.08	0.08	0.11	0.11
Materials								
Operating supplies—5% of labour	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Maintenance materials—1.5% investment/year	0.44	0.44	0.45	0.45	0.44	0.44	0.55	0.55
Catalysts and chemicals	0.65	0.65	0.25	0.25	0.65	0.65	0.25	0.25
Plant overhead at 60% of labour and supervision	0.32	0.32	0.43	0.43	0.32	0.32	0.43	0.43
Indirect taxes								
Local taxes and insurance at 2%/year	0.59	0.59	0.60	0.60	0.59	0.59	0.73	0.73
Return+recovery of investment	4.64	4.64	4.80	4.80	2.14	2.14	2.69	2.69
Interest on working capital	0.50	0.68	0.57	0.72	0.09	0.14	0.10	0.14
Federal income tax	3.41	3.58	3.57	3.71	0	0	0	0
Manufacturing cost, \$/ton NH_3	19.20	26.15	22.07	27.77	12.88	19.53	15.07	19.99

Current costs for commercial tank type and bipolar electrolysis cells, capable of supplying hydrogen to ammonia plants in the range of 300 t/d to 1,500 t/d, obtained from the manufactures suggest increase in cell costs for plants up to 3,000 t/d would be nearly linear as the normal arrangement would be to increase the number of cells, rather than the size of individual units. However the pumps, piping, instruments, scrubbers and solution make up facilities make up the major fraction of the electrolytic plant costs and they can be scaled to 0.6 to 0.7 factor. Capital costs for the commercial cells are almost equal. The relationship between cell capital cost and current density is not linear, however, as is the scale-up to larger capacity plants at constant current density. When the current density is increased at constant capacity, proportionately fewer cells are needed, but the flow clearances between electrodes must be increased to accommodate the increased electrolyte and gas flow rates. The copper busbars, electrolyte and gas piping must be increased for the higher current, liquid and gas flow rates.

Summaries of the costs per ton of ammonia in a 3,000 t/d plant for both steam methane reforming and advanced cell type electrolysis at 4% and 15% return on investment are given in Table II. For the electrolytic process to be competitive with steam mathane reforming the production costs for the ammonia must be equal in the same size plant at equal return on investment. In 100 t/d electrolysis plants, 1.6 mills/kWh power with no oxygen credit, would be competitive with natural gas at 45 C to 47 C/m Btu's.

In large plants the electrolytic route becomes slightly more competitive with the break even point between 41 C and 44 C/m Btu's of gas. For off-peak power conditions, ammonia from nuclear power would be competitive with gas at 38 C/m Btu in a 3,000 t/d plant at 10% return on investment, and with gas at 30 C/m Btu's for 4% return on investment.

Significant cost reductions are expected to be possible through the use of low cost power, locally available raw materials, large production, rates and a highly integrated facility in a multipurpose atomic reactor complex. Nitric acid can be manufactured from ammonia.

[Brit. Chem. Engng. **12** (3), (1967), 319]

News in Brief

Price of Imported Potassium Sulphate

The pool issue price of imported sulphate of potash has been fixed by the Government of India at Rs. 585.00 per metric tonne (gross, F.O.R. ports/despatching station) freight paid by Central Fertilizer Pool up to railhead destination for supplies to State Governments and Union territories.

[Letter No. 2-19/66-MAI dt. 29th May 1967 of Union Ministry of Food, Agriculture, C.D. and Co-operation]

Ureaphoska

Work at the Institute of Artificial Fertilizers at Tarnow (Poland) has resulted in the trial scale production of a new granulated complex fertilizer—named as ureaphoska—based on urea and containing N, P_2O_5 and K_2O in the ratio 1 : 0.7 : 1 and a total nutrient content of 37 per cent. In contrast with other complex fertilizers of the nitrophoska type which contain 50 per cent or less of water-soluble P_2O_5, ureaphoska contains about 90 per cent nitrogen, 40 per cent nitrogen is in the nitrate form.

The high solubility of the phosphate in ureaphoska is produced by the decomposition of the phosphate rock into monocalcium phosphate by nitric acid after which 4 mols of urea are introduced per 1 mol. of P_2O_5 and the potash salt. The method is economical in its use of nitric acid.

[*NPKS Abstrs*, Nov/Dec. (1966), 6]

Coal Fertilizers on Paddy and Wheat

The results of investigations carried out by the Central Fuel Research Institute, Dhanbad (India) at Dhanbad and Hazaribagh with paddy and wheat from 1958-59 to 1963-64 using nitrogen-enrich coal, ammonium sulphate, ammonium humate and organic manure have shown that though ammonium sulphate gave the highest yield for the first two years of application, from the third year onwards coal fertilizers and organic manure gave more yields. This may be explained in terms of the residual effect as well as the humus content.

[*Indian J. Agronom.*, **11** (2) (1966), 193]

World Food and Agriculture Situation

According to a paper submitted to the 47th session of FAO Council held in October 1966, agricultural export earnings, which declined slightly in 1965, appear to have increased in 1966. The value of the agricultural imports of the major trading countries was substantially higher in the first half of 1966 than in the corresponding period of 1965 and the average level of world prices for agricultural products has also increased.

In western Europe production started only slightly in 1965-66. In the U.S.S.R., the grain crop was reported to be 160-165 m. tons in comparison with the poor crop of 120 m. tons in 1965. In 1966-67 wheat harvest in N. America is expected to reach 57 m. tons, a substantial increase in Canada offsetting a 2 per cent reduction in U.S.A.

In the Far East, the output of rice will probably be higher than in 1965-66 with estimated larger crops in Thailand, India and Japan, although recent floods in a number of countries leave the overall situation uncertain. Pakistan's wheat crop is down again as is that of Japan. The final figure of foodgrain production (including pulses) in India in 1965-66 is now put at 73.3 m. tons compared to 89 m. tons in 1964-65.

[*FAO Monthly Bull. of Agric. Econ. & Stat.*, **15** (11))1966), 1]

Steam-Reforming Process

A new steam-reforming process has been developed by the Institute of Gas Technology, Chicago, which is very similar to the one developed by the British Gas Council. It results in a high Btu fuel gas, hydrogen or both. The method employs a highly active nickel-alumina catalyst, which features reduced reaction time and boosted conversions. The possible feedstocks are those having wide range of hydrocarbon types and molecular weights.

[*Hydrocarbon Processing*, Nov. 1966]

North Sea Gas

The Chairman of the Gas Council, U.K. stated that the 18 in. trunk line from Convey Island (near London) to Yorkshire will be linked to the undersea pipelines bringing gas from North Sea and possibly from or to the continent. It may in time also be linked to additional liquefied natural gas, and, in any case, the Convey Island terminal has been designed for such expansion. A recent survey of a pipeline route under the North Sea from Holland to East Anglia (U.K.) had shown that pipelines would be practicable and could be reasonably economic, therefore it is physically possible that U.K. may be linked to a European Gas-pipeline system. The Gas Council is also satisfied that there will be enough North Sea gas for supplying to all area boards through pipelines, which will then be used in various ways—as an enricher for lean gas; a feedstock for reformers; for direct supply to new industrial consumers and to new towns or new districts of old towns and to supply existing gas consumers direct.

[*Chem. in Brit.*, **2** (8) (1966), 370]

Ramgarh Industrial Complex

The possibility of a coal-based industrial complex at Ramgarh (in S. Bihar) was originally envisaged by the Central Fuel Research Institute in 1958, which was to be based on exploitation of semi-coking coal of Karanpura coalfield through medium temperature carbonization integrated with pig iron (by low shaft process), industrial gas, etc. The Ramgarh coalfield, about 94 sq. km. in area, is situated in Hazaribagh district and the neighbouring Karanpura coalfield is just 4 miles away. The National Coal Development Corporation have planned to beneficiate the entire output from their new colliery at Ramgarh. Water will be supplied from the Tenughat dam or a barrage further upstream on *Damodar* river.

A feasibility report covering the possibility of setting up an industrial complex based on maximum utilization of Ramgarh Block I coal has recently been prepared by C.F.R.I. The study has indicated that the coke oven project (4,000 tons/day dry coal throughput) can only be economical provided the entire coke oven gas (or at least the surplus 60 per cent) is converted into fertilizers. The processing of the other byproducts (tar, benzol, etc.) can be undertaken which will reduce the cost of coke. The study also suggests that in the second phase, low shaft furnaces may be built in order to utilize the small size coke for pig iron production. This stage will make blast furnace lean gas available, which can be used for heating coke ovens, thus releasing the entire coke-oven gas for ammonia synthesis. Among the major products for sale, will be urea.

The electric power, consumption of which will be about 60 MW in the final phase, can be supplied either from the proposed Tenughat power station (500 MW) or the existing Patratu power station. The requirement of the substantial quantities of oxygen for the fertilizer plant can be met from the proposed heavy water plant which can be built alongside the Tenughat power station. The authors have studied several alternative integrated schemes giving their profitability and economics. The entire economics of the project is dependent on integration with the fertilizer plant.

[*FRI News*, **16** (2) (1966), 52-56]

Extracting Phosphoric Acid

In a new method of extracting phosphoric acid various dialkyl and diaryl sulphoxides are recommended as selective solvents for extracting the solutions provided by the action on natural phosphates of hydrogen chloride or sulphuric acid. The advantage of the solvents is that they can be recovered and recycled. Generally the extract containing the phosphoric acid is treated with water, yielding the solvent which is recycled, and an aqueous phosphoric acid solution which is concentrated and possibly purified in a furnace.

[*ECN*, **11** (268) (1967), 44]

Mixed NP Fertilizer

Ammonium nitrate and ammonium phosphate mixtures having a water content below 5 per cent are prepared by reacting gaseous ammonia with two or more of the following components: nitric acid, phosphoric acid, ammonium nitrate and ammonium phosphate, selected such that both nitrate and phosphate radicals and an acid are present. The reaction is carried out in a medium comprising previously formed product having a water content between 2 and 10 per cent. This medium is kept at its boiling point by the heat of reaction, while its pH is kept between 2.0 and 2.8. Part of the reaction mixture is withdrawn and is reacted counter-currently with gaseous ammonia, preferably in admixture with an inert gas, at a temperature between 140° and 190°C. This reduces the water content to between 0.1 and 0.5 per cent by weight and adjusts the pH of the final product between 3.0 and 6.0.

[ECN, **11** (268) (1967), 44]

Effects of Nitrates on Farm Animals

It has been believed that sublethal levels of nitrate in forage will cause various adverse effects in farm animals. Investigators from Cornell University have disproved this belief, but nevertheless warn that forage high in nitrate content can kill cows and sheep. The use of nitrogen fertilizer to increase grass and crop yields and corn-feeding are increasing the level of danger. Green crop feeding is reported by a Cornell agronomist, Prof. Madison J. Wright, as being more dangerous than other systems, as the plant is usually nearer the peak of nitrate content when cut.

Feed crops such as corn, oats and sorghums and some weeds can "store" nitrate and if eaten in large quantities within a short period, ruminant animals can suffer acute nitrate poisoning resulting in death.

In a wide investigation, the Cornell workers have shown that sublethal doses of nitrate were decisively negative, with animals showing normal milk production, usual gains in weight and giving brith to healthy calves. Similar tests were conducted on sheep.

When nitrate is eaten it passes readily through the stomach wall, is carried by the blood to the kidney, and finally excreted. In ruminants such as cows, sheep and goats, however, the bacterial flora of the rumen simultaneously reduce some of the nitrate to nitrite. This latter product passes into the blood where it reacts with haemoglobin to block the oxygen-transport system.

Feeds with less than 2% nitrate are unlikely to be fatal, but the rate of consumption is crucial. One half ounce of nitrate per 100 lb. body weight, when poured down the throat, could kill the animal. When the same dose is contained in forage that takes some hours to eat, is relatively harmless.

[*The World of NPKS*, No. 7, Jan. 1967]

Nitrogen Manuring of Potato Crops

Early-planted crops are more responsive to nitrogen than the late-planted ones. This is due to the effects of temperature and nitrogen on the distribution of dry matter; delay in planting (effectively increase in temperature) and increase in N level both increase the proportion of the total assimilate, which is used for haulm growth, and a corresponding decrease in the proportion used for tuber growth. Application of N increases leaf area, usually leading to the production of more dry matter and to greater yields.

Application of part of the N requirements of potatoes in the form of a top dressing after tuber initiation has generally proved to be less effective in increasing yield than seedbed application. Such top dressings may not be washed into the soil, and in any event the pattern of growth is largely established by the time of tuber initiation, and the capacity to respond to N is much reduced.

(University of Nottingham, Report of the School of Agriculture, 1965, p. 29).

[*The World of NPKS*, No. 7, January 1967, 26]

Liquid Nitrogen Fertilizers

Liquid nitrogen fertilizers have gained popularity all over the world. Particularly in regions where agricultural labour costs are high, the liquid fertilizers are welcomed because of their ease of handling and application, high profitability, adaptability to blending with other agricultural chemicals and evenness and accuracy of application. The elimination of on-farm storage and handling problems associated with solid fertilizers, such as the need for dry storage and the danger of over purchase and subsequent product deterioration, has also constituted an important growth incentive for liquids.

Liquid can also be easily transported and cleaning of the tanks is generally straight-forward since simple flushing is

adequate, involving the mere substitution of one liquid for another. These factors have been decisive in promoting liquid fertilizers usage to its present level of over 14% of the world fertilizer nitrogen market. The following recent technological advances have been made by the T.V.A. in the field of liquid fertilizers in industry:

[*Nitrogen*, **45**, Jan-Feb., 1967]

Nitrogen Suspension

A 37% N urea-ammonium nitrate suspension fertilizer has been developed by TVA with the following composition and properties: Urea (%) 57.5; Ammonium nitrate (%) 31.5; Clay (%) 1.0; Water (%) 10.0; Viscosity (cP at 80°F) 246; Density (lb/gal. at 80°F) 11.1; and pH 7-8.

A major advantage of such a product compared with anhydrous ammonia is that because of its high concentration and density it is possible to store a larger amount of nitrogen in a given storage volume with the suspension than with the less-dense anhydrous ammonia. In a 1,000-gal. storage tank only 3,568 lb. of nitrogen as ammonia can be stored, since safety precautions permit only an 85% utilization of the storage capacity, whereas 4,107 lb. of nitrogen as 37% N suspension can be stored in a similar-sized tank.

With its lower-cost shipping and since the clay in the nitrogen suspension is a suitable source for part of the clay for an NPK suspension, the 37% N product has especial value for the preparation of NPK suspensions. Formulations such as 15-15-0, 20-10-10, 5-15-30 and 16-16-8 have already been prepared.

One disadvantage with the nitrogen suspension is crystal growth during storage, which makes storage inadvisable during winter, unless the product is diluted to 28% N. Research work on the suspension is continuing in order to improve its characteristics.

[*Nitrogen*, **45**, Jan-Feb., 1967]

Anhydrous Ammonia-Sulphur Solutions

Results of a pilot plant built by the TVA for research into the production of ammonia-sulphur solutions with a sulphur content of 10%, have shown that molten sulphur could be satisfactorily dissolved in anhydrous liquid ammonia in a continuous process and that during mixing there was no significant variation in the temperature of the anhydrous ammonia. No corrosion was apparent on the plant of the tank built of carbon steel where ammonia sulphur solution was stored, showing that the solutions were stable and could successfully be stored in mild steel tanks for 6-8 months.

[*Nitrogen*, **45**, Jan.-Feb., 1967]

Incorporation of Micro and Secondary Nutrients in Liquids

Small-scale tests were made of the dissolution of several micronutrients—zinc, copper, manganese and iron—in ammonia/ammonium nitrate solution, urea/ammonium nitrate solution and anhydrous ammonia, by mixing at 80°F for about 15 minutes.

In ammonia/ammonium nitrate solutions, it was found that oxides of zinc and copper were generally more soluble than the respective sulphates. Solutions containing 35% N and 5% Zn or 2.5% Cu were prepared with zinc oxide or copper oxide with salting-out temperatures of 76 or 67°F. Oxides or sulphates of other micronutrients, such as manganese and iron, were, however, not soluble in the ammonia/ammonium nitrate solution. Tests with ammonium nitrate/urea solutions showed that, whereas pH of the solutions was significantly lowered by the addition of zinc/copper oxides/sulphates and only zinc sulphate was soluble to any extent, larger amounts of the zinc or copper were soluble when sufficient ammonia was added to maintain the pH of the solution at 7 to 8. Solutions containing 28% N and 5% Zn were produced with zinc oxide and zinc sulphate, with respective salting-out temperatures of 8 and 10°F. Using the 28% N urea/ammonium nitrate solution, a liquid containing 0.5% Cu was obtained by adding copper oxide or sulphate together with ammonia; salting-out temperatures were, however, much higher (64°-70°F) than that of the micronutrient-free solution (−1°F).

Manganese and iron oxides were not soluble in urea/ammonium nitrate solutions even with the addition of ammonia. Iron nitrate or sulphate, without the addition of ammonia, produced solutions containing 0.5 and 0.1% Fe but their pH was very low (about 3). Neither zinc oxide nor copper oxide was soluble in liquid ammonia unless ammonium nitrate was added to the mixture. Solutions containing 2% Zn or Cu and 78% N were, however, produced when 2 moles of ammonium nitrate was added per mole of Zn or Cu.

[*Nitrogen*, **45**, Jan.-Feb., 1967

Addition of Micronutrients to Suspension Fertilizers

No inherent problem of solubility occurs when it is desired to incorporate micronutrients to suspension fertilizers, but the viscosity of the end-product related to the type of application equipment used provides an effective limitation to the amount that can be added. Using a 15-15-15 suspension a range of products containing micronutrients have been produced, such as the 14-14-14-2.5 Zn (zinc sulphate) and the 15-15-15-0.34 Mn (manganese sulphate).

Investigations have recently been made into the incorporation of secondary nutrients in suspension fertilizers and small-scale tests are being carried out with sulphur and magnesium. Using crushed sulphur with a 1-1-1 ratio suspension, grades such as the 12-12-12-20 S and 14-14-14-10 S were produced, the sulphur apparently not reacting with the suspension. Eight different magnesium compounds were tested to produce a 3-2-2 ratio product containing 3% Mg, but in all cases the suspending agent in the 12-40-0 base solution was not sufficient to prevent salting of solids, and additional clay was added to a total of 2% of the final product.

[*Nitrogen*, **45**, Jan.-March, 1967]

Suspension Fertilizers from Phosphate Rock and Nitric Acid

Despite the fact that there is now some commercial production of suspension fertilizer based on the reaction of phosphate rock with nitric acid, TVA has continued to study the potentialities and production methods of these types of fertilizers. An overriding advantage of the nitric/phosphate suspension is the low material cost, since nitric acid serves a twofold purpose of extracting the phosphate rock and supplying part of the nitrogen in the end-product.

Production of this suspension consists of solubilizing phosphate rock with about 2 moles of nitric acid per mole of CaO, followed by the introduction of ammonia into the extra to reduce acidity. When the amount of ammonia added reaches 0.6 mole per mole of nitric acid, all the phosphorus has been precipitated as dicalcium phosphate and about 60% of the calcium nitrate, produced in the first stage of the process, has been converted to ammonium nitrate. A suspension of about 11-10-0 grade results, but the pH of the product is only 2.5 or thereabouts. By adding more

ammonia, the acidity can be reduced further, but in the process dicalcium phosphate reverts to fluorapatite. One way of avoiding reversion is to add sufficient phosphoric acid to form dicalcium phosphate with all the calcium although this would then reduce the nitric/phosphate's cost advantage.

Recently, attention has been focussed on research into other methods which would allow the production of a nitric phosphate suspension with low acidity and high P_2O_5 solubility. One such method involves the addition of a polyphosphate to inhibit the reversion reaction during ammoniation to pH 7 to 8 using an 11-37-0 ammoniated superphosphoric acid as polyphosphate source.

[Nitrogen, **45**, Jan.Feb., 1967, p. 37]

Sulphur Needs When Using High Analysis Fertilizer

Stunted plants with pale yellow leaves may indicate the need for sulphur. Sulphur deficiency can reduce yields and under extreme conditions plants may even die. Growers who use sulphur-free fertilizer may not notice any problems for a year or so. But once the soil sulphur content in the root zone drops to deficiency levels, symptoms develop rapidly. According to the investigation carried out, yields for first 2 or 3 years of sulphur-free fertilization differed little from yields where sulphur containing fertilizers were used or where gypsum (18 per cent sulphur) was applied as a band application at planting. By the third year, however, cotton seedlings were pale yellow, their growth was slow and some plants died. Application of several sources of sulphur caused the symptoms to disappear within 9 to 21 days, even when the sulphur was applied as laté as the green boll stage. Up to 18 pounds of sulphur applied were effective in raising yields. In other instances, plots receiving gypsum for 3 years produced yield increases of up to 33 per cent from annual applications. On sandier soil up to 32 pounds of sulphur/acre were still increasing yield after 8 years of annual application to cotton grown with a high analysis fertilizer lacking surphur. Heavy soils with a negative sulphur content well up in the soil profile may never develop a need for added sulphur.

[J. G. Futral, Dept. of Agr. Engineering and O. E. Anderson, Dept. of Agronomy Georgia Agr. Exp. Sta., *Crops and Soils Magazine*, **19** (4) (1967), 28]

German Systems Reclaim SO_2

Air pollution can be minimized and sulphur dioxide conserved by incorporating into the design of sulphuric acid plants a double absorption system or a scrubbing system each developed by Chemiebau Dr. A. Zieren GmbH.

The double absorption system, which is already being used in sulphuric acid plants in Lenzing (Austria), Antwerp and Magdeburg, is claimed to reduce sulphur dioxide losses from a 330,000 ton/year plant from 4,300 to 1,000 tons annually.

It is equally suited to recovering sulphur dioxide from off-gases having a high or low concentration of sulphur dioxide.

Water and ammonia are used for scrubbing the sulphur dioxide from the off-gases in the second process, which has been incorporated in sulphuric acid plants at Travancore, Geleen, Wesseling, Worms and Zwickau.

One virtue of the latter technique is that it can be used for recovering sulphur dioxide in the event of a failure in the steam supply putting the absorption system out of action.

Proportion of sulphur dioxide lost to the atmosphere when off-gases from a 330,000 tons/year plant are purified by scrubbing is said to be reduced to 130 tons/year.

[*ECN*, **11** (267) (1967), 34]

Fertilizer in Plastic Packets Keeps Trees Well-fed

In planting a tree or shrub, if an ounce of fertilizer is sprinkled in the hole, the salts in the fertilizer will dehydrate the tender roots and will probably kill it.

But if the same ounce of fertilizer is put in a plastic packet there is no injury, according to the investigation carried out by Wisconsin University scientists. By punching four to eight pinholes in the packet and placing it about 6 inches deep and 6 to 12 inches to the side of the tree or shrub, the packet becomes a self-feeder. It gives the tree a quick start and keeps it well-fed for as long as five seasons. The scientists say that the packets work because what little air there is in the soil is usually near 100 per cent relative humidity. As each drop of the fertilizer-water mixture spills out the moisture in the soil dilutes it to the strength the plants like. Results over the past 5 years indicate that the packets will keep a tree or shrub well-fed for 3 to 5 years.

[*Crops and Soils Magazine*, **19** (4) (1967), 24]

Safer Preheat Air for Ammonia Plants

The compression and preheating of air for the secondary reformer in ammonia plants are potentially dangerous operations —particularly when lubricated reciprocating compressors are used. Among several approaches taken by the Mosanto Co's Muscating, Iowa plant, for making the operations safer the following approach was considered to be successful: (i) A fire resistant phosphate ester type low vapour pressure lubricant was selected for the compressors cylinders. (ii) A glass fiber mist eliminator was installed to handle the air at 250°F and 225 lb/sq. in gauge. The eliminator was designed to remove essentially 100% of all mist particles layer 3 microns in size and 99% of all remaining mist particles which are 3 microns or less.

In one year of operation, this system has had excellent maintenance experience. To ensure safety however, the compressors should be cleaned thoroughly at the beginning of switching from petroleum oil to synthetic lubricant. The new system with the synthetic lubricant has had no detrimental effects on the catalyst or process to date.

[*CEP*, **63** (2) (1967), 83]

New Process for Potassium Metaphosphate

A new process for producing potassium metaphosphate, which involves reacting phosphoric acid and potassium chloride on the surface of a fused salt bath, has been developed by Societe d'Etudes Chemiques pour d'Industrie et l'Agriculture of France. The salt bath contains the final product of the reaction and is maintained at its melting point by the heat supplied to the bath externally and partly from within the bath. A tank furnace—in which the fused salt is maintained near the melting point by means of a burner and partly by the Joule effect, using graphite electrodes connected to a source of electricity—has been employed for maximum heat efficiency; the heat supplied inside the bath is between 10 and 25% of the total heat required, the fused salt bath being kept at temperatures in the range of 650 to 800°C. Use of phosphoric acid of at least 25% P_2O_5 concentration and an equimolecular mixture of acid and potassium chloride is recommended. A water soluble product is obtained by cooling the molten potassium metaphosphate.

[Phosphorus and Potassium, **26** (1966), p. 51]

TECHNOLOGY

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CONTENTS

EDITOR: S. N. ROYE

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EDITOR'S NOTE

It has now been decided to publish in *TECHNOLOGY* research papers from scientists and technologists outside FCI Ltd., provided these are:

(*i*) original and related to fertilizers,
(*ii*) approved by external referees chosen by the Editor and
(*iii*) communicated from reputed institutions, and are written by workers with adequate experience.

Papers for publication in *TECHNOLOGY* are therefore welcome. These should be sent in duplicate (complete with illustrations and abstracts) to the Editor.

Caking in Fertilizers: Pulverized Materials as Anti-Caking Agents

By

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The extent of retention of limestone on spherodized CAN* has been found to depend on the particle size of limestone: The finer the particles the greatei is the retention. Experiments have shown that some of the samples of limestone have greater adhering power than others; soap-stone is retained only to a limited extent. Reasons for low retention of soap-stone have been advanced. The measurement of sedimentation volume reflects the degree of interaction of coating agent with the saturated solution of the fertilizer. Coating agents with low sedimentation volume are more effective in prevention of caking than those which give high sedimentation volume and are of limited wettability. An attempt has been made to calculate theoretically the extent of retention of limestone on CAN and a generalized simple expression is evolved for determining the amount of coating agent required for unilayer coverage of fertilizer granules. A microscopic study of the coated samples has been made.

Early in 1920, Lowry[1] found that caking in ammonium nitrate is caused by recrystallization of the saturated solution of the salt formed on the crystal surface due to the presence of moisture. Later microscopic studies[2,3] have clearly elucidated the mechanism of caking in a fertilizer: the moisture present forms a saturated solution of the fertilizer which gathers, due to capillary forces, at the point of contact of the contiguous particles. Any fall in humidity or temperature of the surrounding atmosphere causes recrystallization which cements the particles together. It is, thus, established that the main cause of caking is the presence of moisture and the caking increases with the increase in moisture content. Pressures to which fertilizers are subjected during storage cause further deterioration of the fertilizer and the cake formed becomes hard. The extent of deterioration of the fertilizer is expected to increase with increase in the ambient temperature because of increased solubility of the fertilizer. This effect is shown to be considerable in the case of ammonium nitrate whose temperature coefficient of solubility is high[4]. The extent to which the above factors affect the keeping quality of the product depends on the nature of the fertilizer and its granulometry. Caking may also occur from causes other than moisture, viz. crystal transformations (in ammonium nitrate) or the formation of new compounds as a result of double decomposition reactions likely to occur in many of the formulations of mixed fertilizers.

Moisture

Caking may occur due to the residual process moisture present in the fertilizer or to moisture which it adsorbs from the surrounding atmosphere. The latter may be effectively checked by dehumidification of the silo where the fertilizer is stored in bulk and by packaging the product in suitable moisture-proof bags prior to its despatch.

It would appear that the production of moisture-free product may be the solution to the problem of caking. As an optimum proportion of liquid phase is essential for granulation, water, therefore, is necessary. The total removal of water is difficult to attain in practice since the rate of drying falls rapidly as the moisture content decreases on account of increasing diffusional resistance offered by the crystal film deposited in the process of drying. Consequently the attempt is always to remove as much moisture as possible by drying and by using various anti-caking agents to neutralize the effect of residual moisture and thus keep the product free flowing.

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* Calcium Ammonium Nitrate

Anti-Caking Agents

There are wide varieties of anti-caking agents in use for conditioning fertilizers. There are hundreds which have either been tried or patented. These additives may be broadly grouped under two categories. The first category may include additives which are required in relatively small amounts, i.e. 0.005-0.1 per cent by weight of the fertilizer. Use of pulverized inert materials to the extent of 2-6 per cent belongs to the second category. The first category includes dyes, surface-active agents and crystal growth inhibitors. The effect of these additives is specific. For instance, acid magenta[2] is known to modify crystal structure of ammonium nitrate IV to a dendritic and fragile form and thus reduce caking, but this dye fails to modify the crystal structure of ammonium nitrate III stable above 32°C. Surface-active agents of long chain aliphatic amines and their salts are stated to be effective as anti-caking agents for straight fertilizers such as potassium chloride, ammonium chloride and ammonium nitrate. These additives reduce the surface tension of the saturated solution of the fertilizer. Reduction of capillary forces reduces the volume of crystal deposited at the points of contact of the fertilizer particles[5]. The efficacy of surface-active agents, however, is still in doubt.

A recent interesting development in this field is the inhibiting effect of small quantities of certain chemicals on the crystal growth of many substances[6]. Such crystal growth inhibitors have been found to be effective anti-caking agents since they tend to suppress crystallization: 0.1 per cent ferric chloride is shown to inhibit crystal growth and reduce caking in ammonium sulphate. Cadmium chloride is found effective in the case of ammonium chloride. One of the limitations to the utility of such additives is that they prevent crystal formation due to the drop in temperature but are of little value when the caking occurs due to the fluctuation in humidity. Moreover, their effect is specific, and the effectiveness of such additives has been established only for straight fertilizers.

Pulverized Materials

The more common and widely used method to minimize caking in fertilizers is to coat the product with 2-6 per cent by weight of inert, pulverized materials. Prominent materials belonging to this group are: kieselguhr, limestone, dolomite, kaolin, soapstone, river clay, gypsum, plaster of paris, precipitated chalk, tricalcium phosphate, etc. The surface coating of the fertilizer granules by such inert powders is achieved by adding them to the granular product in the rotary drum. The individual granules thereby get coated with the particles of the powdered material. These pulverized materials tend to absorb the saturated solution of the salt, thus making it unavailable for the formation of intergranular bridges. The coating by inert material also prevents the granules of the salt coming into direct contact with each other[2]. It has also been shown that coating agents prevented localized growth of crystals between contiguous granules[3]. Kumagai and Hardesty[7] tried the effect of 17 different materials as coating agents on a 12-12-12 fertilizer and found that materials of extremely low bulk density viz., hydrated silica, synthetic calcium and magnesium silicate and kieselguhr were most effective. High bulk density materials were found to be least effective.

Even though a large number of coating agents were tried in this laboratory for fertilizers such as calcium ammonium nitrate (CAN), ammonium sulphate-nitrate and nitrophosphate the choice was in fact limited. Some of these were not as effective in preventing caking and the rest were of theoretical interest only because of excessive cost. Kieselguhr, on account of its extremely low bulk density and high oil absorbity, is a versatile and effective coating agent and is widely used in the western countries. Since it is not available indigenously our attempt has been to replace it with an available substitute.

Retention

In order for coating agents to be fully effective, it is necessary that the fertilizer granules are coated uniformly and the pulverized material remains adhered to the granules. The importance of particle size of the coating agent in this context has been stressed earlier[8]. Experiments have been conducted to determine the influence of particle size of limestone on the extent of retention on spherodized, uncoated calcium ammonium nitrate. The amount of coating agent retained has been determined by adding an excess of coating agent (8 per cent by weight) to CAN accurately weighed granules in a bottle which is then rapidly rotated and the granules are weighed. Next the coated sample is sieved for 10 mins. on a 40 mesh (B.S.) screen and finally weighed. The amount of coating agent retained is the difference in weight between coated and uncoated sample. The percentage retained after sieving is taken as the amount of coating agent held firmly by CAN and is expected to survive the agitation normally met with during handling and transport of the coated product. Caking tests were performed with spherodized CAN of 2-3 mm. diameter. The percentage reduction in the crushing strength of the cake is taken to mean the probable im-

provement in the storage properties of the fertilizers. The crushing strength of the uncoated CAN containing about 0.8 per cent moisture is 7.0 Kg/cm^2. The detail of the caking test method is described elsewhere[4]. The crushing strength values are average of six determinations:

TABLE 1

Sample	Particle Size mesh (B.S.)	% Retained before Sieving	% Retained After Sieving	% Reduction in Caking
Limestone	100 to 200	2.2	1.3	15
-do-	200 to 300	4.1	2.1	20
-do-	100% passing thro' 200	7.5	3.9	60
-do-	100% passing thro' 300	8	4.1	65
Soapstone S_2	100% passing thro' 300	1.2	0.6	20
†Limestone L_1	100% passing thro' 200	0.8	0.6	10

†In this case 0.8 per cent by weight of limestone was used for coating.

Results indicate that the finer the particles the better is the retention. There is, however, a small difference in the extent of retention and reduction in caking between particles of coating agent passing through 200 and 300 mesh. The retention of soapstone to CAN is found to be much less than that of limestone. This limited retention of soapstone on calcium ammonium nitrate is chiefly due to the weak interaction of soapstone particles with water or the saturated solution of ammonium nitrate as a result of which it is not wetted easily. When a small quantity of soapstone is added to water or saturated solution of ammonium nitrate it floats at the top without getting wetted or dispersed. Only after vigorous shaking does the soapstone sink to the bottom. On the other hand, limestone, kieselguhr and kaolin immediately disperse in the solution and settle at the bottom. For the same reason sedimentation volume as determined by shaking the pulverized material with saturated solution of the fertilizer in a graduated cylinder, allowing it to settle, and then recording the level of liquid phase, is more in the case of soapstone than with limestone, kieselguhr or kaolin. A low sedimentation volume indicates stronger interaction and increased wettability of coating agent particles with the saturated solution of the fertilizer. Another evidence is that the anti-caking effect of soapstone appears to be out of proportion to the extent of its retention on the surface of CAN granules. This may be because soapstone, since not easily wettable, acts as a buffer and prevents the granules from coming into direct contact with each other. Limestone, on the other hand, absorbs the saturated solution of the fertilizer and thus prevents the intergranular leakages. As the results indicate, at low concentration of the coating agent, i.e. 0.6 per cent, when the surface is partially coated the buffer action of soapstone appears to be a more significant factor in reducing caking than any reduction due to the absorption capacity of limestone.

In another set of experiments the extent of retention was determined with different samples of limestones. As the results (Table 2) indicate, the extent of retention varied with the type of limestone. Of the 10 samples of limestone used as coating agents, all fall broadly into two groups: the extent of retention of one group being nearly twice that of other group. Some typical results are given below (Table 2), and all the varieties of limestone fall in line with samples L_1, L_2 or L_3 & L_4. This difference with regard to adhesive property is strange and the analyses of these samples failed to provide any clue for the difference with respect to retention. There is in fact greater similarity between samples L_2 and L_3 than between L_1 and L_2, as far as chemical composition is concerned.

TABLE 2

Sample	% Retained Before Sieving	% Retained After Sieving	Analysis
Limestone (L_1)	7.5	3.9	Loss on ignition, 42.2; CaO, 37.1; MgO, 11.5 SiO_2 & other acid insolubles 6.2; R_2O_3, 2.7
Limestone (L_2)	6.9	3.8	Loss on ignition, 43.2; CaO 52.3; MgO, 1.81 SiO_2 & other acid insolubles, 1.8; R_2O_3, 0.9
Limestone (L_3)	3.6	1.9	Loss on ignition, 42.1; CaO, 49.3; MgO, 2.9 SiO_2 and other acid insolubles, 3.7; R_2O_3, 1.4
Limestone (L_4)	3.8	2.1	Loss on ignition 42.7; CaO, 46.8; MgO, 4.9 SiO_2 and other acid insolubles, 4.0; R_2O_3, 1.2

Granules of irregular shape obtained by breaking large spherodized granules into smaller pieces, 2-3 mm. in diameter, were able to retain a larger amount of limestone samples L_3 and L_4, i.e. 2.8 and 2.7 per cent, in place of 1.9 and 2.1 per cent respectively, as shown above for regular spherical granules. There was, however, a small increase, from 0.6 to 0.8 per cent, in the case of soapstone. Low retention for the limestone samples is partly due to the smooth and dense surface of spherodized CAN. Broken irregular shaped granules having a rough surface with crevices are capable of retaining a larger amount of coating agent.

Theoretical Requirement

The extent to which a coating agent is retained by the fertilizer, as indicated earlier, depends on its adhesive power with respect to the fertilizer in question and its particle size and can easily be determined in the laboratory. The addition of a large excess of coating agent is of little value since the excess segregates and leads to the loss of coating material and creates a dust nuisance. An attempt has been made for the first time to calculate theoretically the requirement of coating agent for the mono-layer coverage of the surface of spherodized CAN. The value obtained may be taken as the minimum of a coating agent required, since in actual practice multilayer coverage cannot be totally avoided largely because of increased adhesive forces between particles of smaller dimensions, i.e. less than 15μ. The calculations have been made for limestone sample L_1 as coating agent which is of distinct colour and possesses good adhesive property.

Assuming that CAN granules and limestone particles are spherical, the effective surface area of one CAN granule of average diameter 3 mm. will approximate (since r_1/r_2 is very large)

$=4\pi\,(r_1+r_2)^2$ where r_1 and r_2 are the radii of a CAN granule and limestone particle, respectively.

$=4\pi\,(0.15+18\times10^{-4})^2$

$=0.2896$ sq. cm.

Projected area of one limestone particle of mean diameter 36μ on the surface of CAN granule.

$=\pi\, r_2^2$

$=3.142\,(18\times10^{-4})^2$

$=10.18\times10^{-6}$ sq. cm.

Placement of spherical limestone particles on the surface of a CAN granule would leave voids and these have to be taken into consideration by calculating void area and the value added to the projected area of limestone in order to obtain the effective area covered by the projection by one limestone particle. The area of void is indicated by the shaded portion in Fig. 1 arising out of closest packing of spheres.

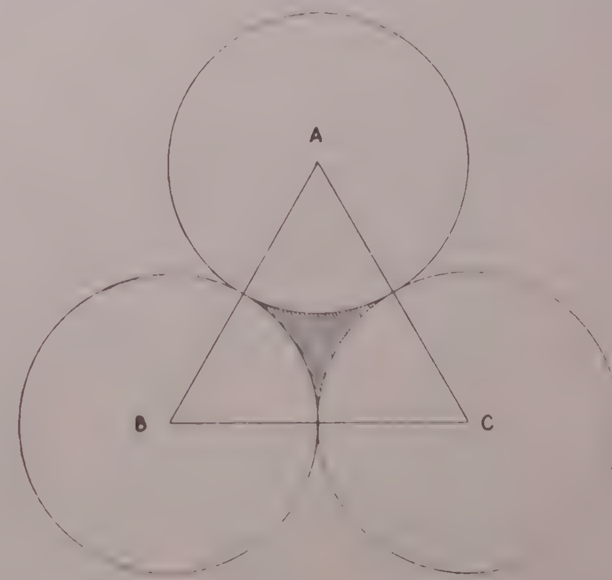

Fig. 1

Area of void $=$ The area of triangle ABC—Area of three 60° angle segments.

$=\frac{1}{2}$ base $\times$ height$-3\times\pi r_2^2/6$

$=\frac{1}{2}2r_2\times r_2\sqrt{3}-\frac{1}{2}\pi r_2^2$

$=r_2^2\,(\sqrt{3}-\pi/_2)$

$=(0.0018)^2\,(\sqrt{3}-3.142/2)$

5.217×10^{-7} sq. cm.

The number of voids resulting from the closest monolayer packing may be taken as n-2, where n is the number of limestone particles. As n is very large, the number of voids can be taken as the number of limestone particles.

Effective projected area of one limestone particle

$=$ projected area of limestone particle $+$ area of a void

$=10.18\times10^{-6}+5.217\times10^{-7}$

$=10.702\times10^{-6}$

The number of particles required to cover one CAN granule

$$=\frac{\text{Effective surface area of one CAN granule}}{\text{Effective projected area of one limestone particle}}$$

$$=\frac{0.2896}{10.702\times10^{-6}}$$

$=2.706\times10^4$

The number of particles required to cover 1900 granules of CAN weighing 100 g.

$=2.706\times10^4\times1900$

$=5.142\times10^7$

Percentage by weight of limestone required

$$=\text{number of particles} \times \text{volume} \times \text{density}$$
$$=5.142 \times 10^7 \times 4/3 \times 3.142\ (18 \times 10^{-4})^3 \times 2.6$$
$$=3.27$$

Neglecting voids, general expression for the percentage requirement of coating agent may be written in the form:

$$\frac{V}{s}\ d.A.N.$$

where V = volume of a particle of the coating agent
s = projected surface area of the coating agent particle.
d = density of the coating agent
A = Effective surface area of one granule
and N = number of granules per 100 g. of the fertilizer

$$=A \times \frac{4}{3} N \times r \times d$$

where r = radius of the coating agent

The requirement (in percentage) of limestone from the above expression

$$=0.2896 \times 4/3 \times 1900 \times 0.0018 \times 2.6$$
$$=3.43$$

The difference of 0.16 per cent arises on account of voids. From the above expression, it follows that the finer the particles of coating agent and the lower its density the less will be required. This explains the fact that the amount of coating agent required for the adequate coverage of fertilizer granules by low-bulk density materials is less than by high-bulk-density materials.

Distribution of Coating Agent

For the microscopic study of the distribution of a coating agent on the surface of ammonium nitrate, Whetstone[9] coated ammonium nitrate with pigments. He found that the retention of pigment of dry ammonium nitrate was poor and tended to occupy the interstitial spaces on the surface of fertilizer granules. He assumed that a coating agent behaved in a similar fashion. In the present study we are fortunate that one of the limestone samples, i.e. L_1, possessing good adhesive property was of pink colour and provided excellent contrast on dark grey CAN granules for microscopic study. The coated granules prior to sieving were observed through the microscope and they showed a uniform multilayer coverage. An agitation given to the granules by sieving removed excess of limestone held less firmly, and the microscopic study after agitation revealed a nearly unilayer coverage. Distribution of soapstone on spherodized calcium ammonium nitrate was found to be irregular and only in patches, and the coating agent remained in the crevices and in the relatively rough portion of the surface. Soapstone being white also contrasted with the dark surface of CAN.

Conclusion

It is believed that the coated product does not and should not cake. This is not quite correct. The reason is that the efficacy of coating agents, such as limestone, kieselguhr, kaolin, etc., depends largely on their ability to absorb the saturated solution of the fertilizer, and once their absorption capacity is reached the coated product fares no better than the uncoated ones. Coating of the product by pulverized material thus is no substitute for efficient drying or proper packaging and is effective only when the moisture content in the product is within tolerable limits.

Acknowledgement

The authors' thanks are due to Dr. K. R. Chakravorty, General Manager, P & D Division, for his active interest in this work.

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Hydrodesulphurization of Petroleum Feedstock Part III—Kinetic Study of Hydrotreatment of Heptane Solution by Ethylmercaptan

By

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Ethyl mercaptan in heptane solution has been hydrogenated in vapour phase over cobalt molybdate catalyst in a bench scale unit. Temperature, heptane and hydrogen feed rates have been varied widely under atmospheric pressure operation. Based on the experimental data a satisfactory kinetic expression has been obtained. Allowable space velocities for 99 per cent conversion of ethyl mercaptan into hydrogen sulphide have been predicted and compared with those for conversion of carbon disulphide, thiophene and dibenzothiophene. The velocity co-efficients and energy of activations for hydrogenation of different organic sulphur compounds have also been compared.

Introduction

In our previous publications[1,2] kinetic studies on hydrotreatment of heptane solutions of carbondisulphide and thiophene have been dealt with separately. This paper relates to kinetic study on hydrotreatment of heptane solution of ethyl mercaptan.

Theory

The theoretical kinetic expression for hydrodesulphurisation of organic sulphur compounds has been already derived in our previous publication[1] and the same is reproduced here.

$$-\frac{F}{\bar{W}_R} \ln \frac{X_{S,2}}{X_{S,1}} = K_H e^{-E/RT} \quad X_H{}^m . P \qquad \ldots .(1)$$

Experimental

Set-up and Procedure: The bench scale unit consists of equipments already used in our previous studies[1,2] on hydrotreatment of heptane solution of carbondisulphide and thiophene.

Materials Used

(*a*) Heptane, chemically pure

Sp. Gr.	— 0.69
Boiling Pt.	— 98°C
Sulphur	— nil.

(*b*) Ethyl mercaptan, chemically pure

Sp. gr.	— 0.839
Boiling Pt.	— 35.04°C

(*c*) Cobalt molybdate catalyst pellets (prepared in this Laboratory)

Size	— 6 mm. diam. ×9 mm. long
CoO	— 2.5%
MoO_3	— 5.0%
NiO	— 0.25%
Al_2O_3	— rest

Since the charge of catalyst, used in the previous studies on hydrotreatment of heptane solutions of carbon disulphide and thiophene respectively, retained its full activity, the same was kept in a place inside the reactor tube; the present study was carried out using the above charge of catalyst. The operational procedure is the same as before, but since the catalyst charge was

in a sulphided state from the initial stage about 10 hours were found to be sufficient for the catalyst activity to reach an equilibrium value. Experimental data were collected after the activity of the catalyst reached a steady equilibrium value under any experimental condition.

Estimation of Sulphur Compounds: Quantitative estimation of mercaptan sulphur was done by color-indicator method as per ASTM Designation D 1219-61. Hydrogen sulphide in noncondensable gas was estimated by absorbing in cadmium sulphate solution followed by iodometric titration.

Results

Experimental data (Table 1) show the percentage conversion of mercaptan sulphur into hydrogen sulphide at different flow rates and temperatures. 50 g. of cobalt molybdate catalyst presulphided during hydrogenation of carbon disulphide and thiophene were used. Since the present set of experiments were carried out under atmospheric pressure, equation (1) may be expressed as

$$-\frac{F}{W_R}\ln\frac{X_{S,2}}{X_{S,1}} = K_H e^{-E/RT} X_H^m \qquad \ldots\ldots(2)$$

Exponent m was determined by plotting values of $-\frac{F}{W_R}\ln\frac{X_{S,2}}{X_{S,1}}$, g. moles/hr. g. catalyst against X_H, mole-fraction of hydrogen in a log-log graph (Fig. 1).

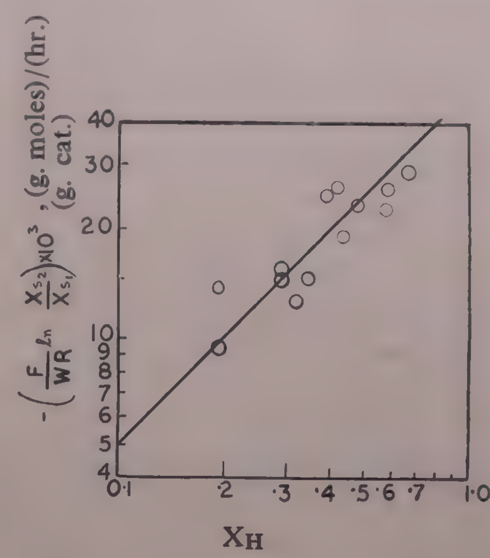

TABLE 1

Expt. No.	W_R, g. catalyst used	F_H, g. moles H_2/hr in Feed	F_{HC}, g. moles heptane/hr in Feed	F, Total Feed, g. moles/hr.	Temp., °C	Mercaptan in Heptane Feed, ppm wt./wt.	Conversion of Mercaptan into H_2S, %
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1.	50	0.205	0.504	0.709	330	5470	64.2
2.	-do-	0.134	0.562	0.696	331	5470	63.4
3.	-do-	0.428	0.563	0.991	332	5470	62.0
4.	-do-	0.715	0.512	1.227	332	5470	61.0
5.	-do-	0.224	0.423	0.647	330	5510	67.5
6.	-do-	0.795	0.560	1.355	331	5510	62.2
7.	-do-	0.417	0.628	1.045	326	5510	71.4
8.	-do-	0.434	0.222	0.656	330	5510	89.2
9.	-do-	0.464	0.492	0.956	331	5510	60.2
10.	-do-	0.413	0.484	0.879	278	5510	36.2
11.	-do-	0.450	0.452	0.902	384	5510	73.0
12.	-do-	0.416	0.493	0.954	407	5510	73.4
13.	-do-	0.457	0.955	1.412	328	5510	36.0
14.	-do-	0.427	0.953	1.380	302	5510	31.0
15.	-do-	0.467	0.339	0.806	225	5180	39.3
16.	-do-	0.417	0.356	0.773	275	5180	94.0
17.	-do-	0.495	0.361	0.856	354	5180	96.2
18.	-do-	0.432	0.284	0.716	381	5180	94.5
19.	-do-	0.473	0.276	0.749	430	5180	94.2
20.	-do-	0.448	0.254	0.702	455	5180	97.1
21.	-do-	0.460	1.131	1.591	323	5180	37.8
22.	-do-	0.391	0.556	0.947	325	5180	75.4
23.	-do-	0.414	1.728	2.142	328	5200	20.3

A straight line relationship was obtained from the slope of which the value of m was found to be unity. The kinetic expression may therefore be stated as

$$-\frac{F}{W_R}\ln\frac{X_{S,2}}{X_{S,1}}=K_H e^{-E/RT}\ .\ X_H \qquad \ldots\ldots(3)$$

To evaluate the values of activation energy E and velocity coefficient k_H, an Arrhenius type of plot was made by plotting values of

$$\ln\left[-\left(\frac{F}{W_R}\ln\frac{X_{S,2}}{X_{S,1}}\right)/\,x_H\right] \text{ g.moles/(hr.) (g. catalyst.)}$$

(molefraction hydrogen) against $\frac{1}{T}$, °K^{-1} (Fig. 2). From the slope and intercept of the straight line obtained (Fig. 2), the values of E and k_H were found to be 3974 g·cal/g. mole. and 1.35 g. moles/(hr). (g. catalyst). (molefraction H_2), respectively. Hence, the experimental data may be correlated with the following expression

$$-\frac{F}{W_R}\ln\frac{X_{S,2}}{X_{S,1}}=1.35\ e^{\frac{-2000}{T}}\ .\ X_H \qquad \ldots\ldots(4)$$

Table 2 represents the values of the functions plotted in fig. (1) & (2).

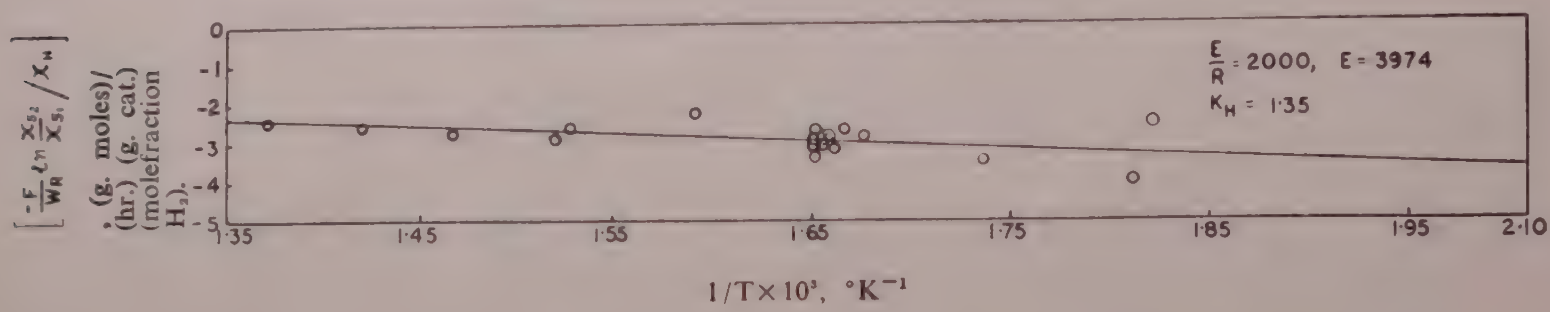

TABLE 2

Expt. No.	X_H, Molefraction of Hydrogen	$X_{S_1}\times 10^4$, Molefraction of Mercaptan in Feed	$X_{S_2}\times 10^4$ Molefraction of Mercaptan in Product	$\frac{10^3}{T}$ °K^{-1}	$\left[-\frac{F}{W_R}\ln\frac{X_{S_2}}{X_{S_1}}\right]\times 10^3$ g. moles/(hr.) (g. Cat.)	$\ln\left[\left(-\frac{F}{W_R}\ln\frac{X_{S_2}}{X_{S_1}}\right)/X_H\right]$ g. moles/(hr.)(g. Cat.) (molefraction H_2)
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1.	0.289	62.6	22.50	1.660	14.50	−2.99
2.	0.193	71.3	26.10	1.655	13.90	−2.76
3.	0.433	50.0	19.00	1.655	19.10	−3.29
4.	0.583	36.8	14.30	1.655	23.00	−3.32
5.	0.346	58.1	18.90	1.660	14.60	−3.15
6.	0.587	36.7	13.90	1.655	26.30	−3.10
7.	0.391	54.1	15.50	1.670	26.00	−2.80
8.	0.663	29.9	3.22	1.660	29.20	−3.10
9.	0.487	45.7	18.15	1.655	23.50	−3.02
10.	0.416	48.0	30.60	1.815	8.17	−4.02
11.	0.500	44.4	12.00	1.523	23,60	−3.04
12.	0.484	45.8	12.20	1.470	25.10	−2.86
13.	0.323	60.1	38.40	1.665	12.40	−3.25
14.	0.308	61.4	42.40	1.740	10.20	−3.46
15.	0.580	35.2	21.20	2.010	8.02	−4.27
16.	0.539	38.5	2.32	1.825	43.50	−2.51
17.	0.579	35.2	1.33	1.595	55.10	−2.34
18.	0.604	33.2	1.78	1.530	41.7	−2.67
19.	0.632	30.8	1.79	1.423	42.7	−2.69
20.	0.638	30.3	0.89	1.375	49.5	−2.56
21.	0.289	59.5	37.0	1.680	15.5	−2.91
22.	0.413	49.3	12.1	1.670	26.6	−2.73
23.	0.193	67.7	54.0	1.663	9.4	−2.91

Effect of Space Velocity on per cent Conversion: The effect of space velocity expressed as g. moles feed (hydrogen+heptane)/(hr.) (g. catalyst) on per cent conversion of mercaptan sulphur into hydrogen sulphide has been shown (Fig. 3). This shows that within the range of space velocities studied conversion is inversely proportional to space velocity.

Discussion

In the present study it may be found from equation (4) or Fig. 2 that under atmospheric pressure operation, the allowable space velocity for 99 per cent conversion of mercaptan sulphur into hydrogen sulphide at 350°C and 0.5 atmosphere of hydrogen partial pressure is 5.74×10^{-3}. g. moles (hydrogen+heptane)/(hr.) (g. catalyst).

From Fig. 1 it is found that space velocity, F/W_R is directly proportional to partial pressure of hydrogen between the range of 0.19-0.67 atmosphere of hydrogen partial pressure. Assuming that this finding is applicable upto 10 atm. of hydrogen partial pressure, the allowable space velocity for 99 per cent conversion of mercaptan sulphur at 0.5 molefraction of hydrogen, 10 atm hydrogen pressure and 350°C may be estimated as 11.48×10^{-2} g. moles (hydrogen+heptane)/(hr.) (g.).(catalyst). Table 3 shows the estimated allowable space velocities for 99 per cent conversion of different organic sulphur compounds into hydrogen sulphide at 0.5 molefraction hydrogen, 10 atm. hydrogen pressure and 350°C. Feed concentration may be 500-3000 ppm. (wt/wt) as sulphur. The same table also shows the values of activation energies and velocity coefficients for these different systems.

Nomenclature

- e = Constant, 2.72
- E. = energy of activation, g.cal./g.mol.
- F = total feed, g.moles (hydrogen+hydrocarbon)/hr.
- F_H = g. moles hydrogen/hr.
- F_{HC} = g. moles hydrocarbon/hr.
- K_H = velocity coefficient, g.moles/(hr.) (g. catalyst). molefraction H_2)
- m = exponent on partial pressure of hydrogen
- P = total pressure, atm.
- R = gas constant, 1.987 g. cal/g. mol. °K.
- T = absolute tempr. °K.
- W_R = wt. of catalyst, g.
- X_H = molefraction of hydrogen
- $X_{S,1}$ = molefraction of sulphur compound at inlet to the catalyst bed.

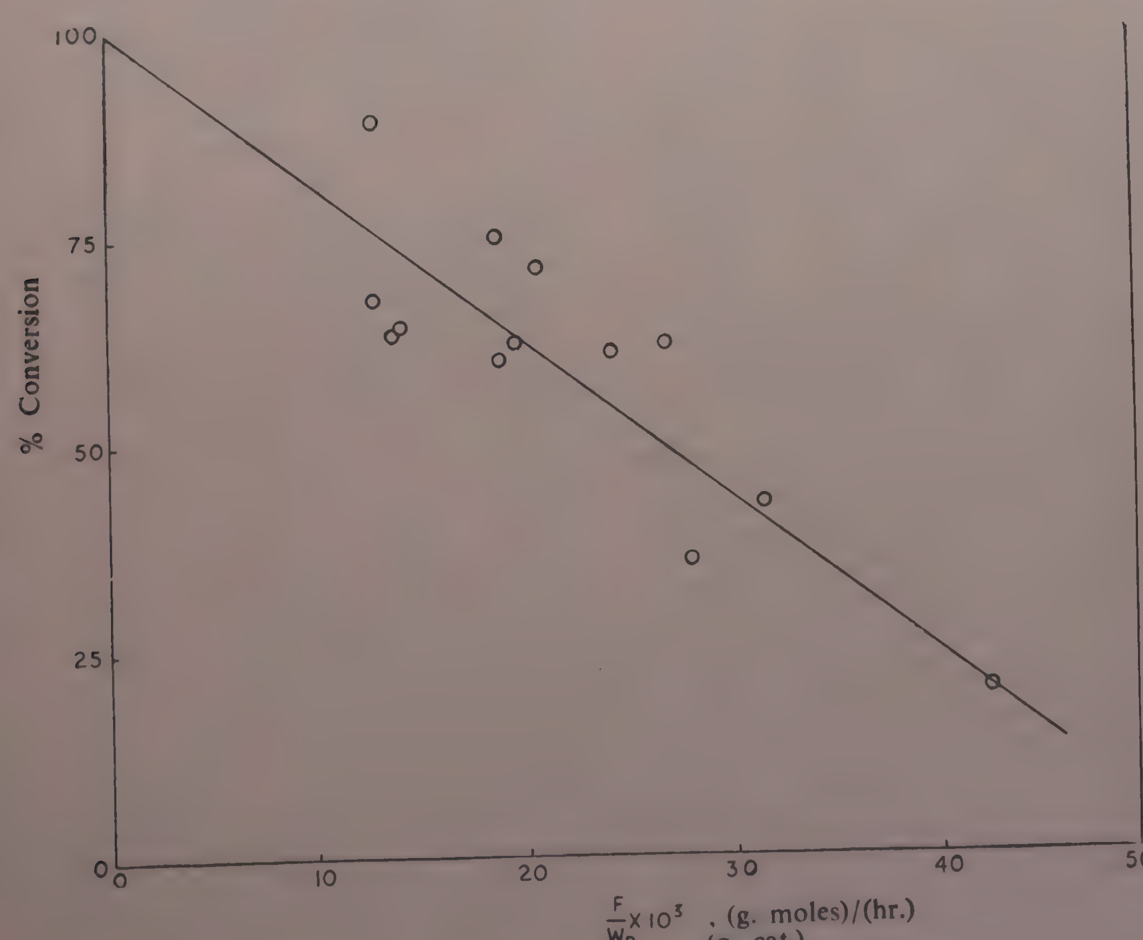

Fig. 3

TABLE 3

Sl. No.	System	Process Condition	Estimated Allowable Space, velocity for 99% Conversion of Sulphur (Compounds into H_2S, g.mol/(hr) (g. cat.)	E, Energy of Activation g cal/g. mole	k_H, Velocity Coefficient g. mole/(hr) (g. cat.) (molefraction hydrogen)
1.	Hydrogenation of CS_2 in Heptane soln. (Ghosal etc)[1]	Molefraction H_2 =0.5 H_2-Partial pressure =10 atm Temp. =350°C	23.3×10^{-2}	2,000	0.532
2.	Hydrogenation of Thiophene in Heptane Soln. (Ghosal etc.)[2]	-do-	4.12×10^{-2}	4,170	0.550
3.	Hydrogenation of Ethyl Mercaptan in heptane solution	-do-	11.48×10^{-2}	3,974	1.350
4.	Hydrogenation of Dibenzothiophene in Naphtha Soln.[3] (Assuming space velocity is directly proportional to partial pressure of hydrogen)	-do-	2.98×10^{-2}	3,800	0.290

$X_{S,2}$ = molefraction of sulphur compound at outlet from the catalyst bed.

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Polarographic Studies on Chromate in Cooling Water

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Polarographic studies with chromate have shown that with 0.1 N sodium sulphate as supporting electrolyte and 0.01 per cent solution of gelatine as maxima suppressor, Cr^{6+} is reduced to Cr^{2+} in distilled water and to Cr^{3+} in water containing various dissolved salts as in the cooling water in a plant. A polarographic method is given for the estimation of chromate in cooling water.

Chromate in combination with sodium polyphosphate is used in the cooling tower water to prevent corrosion and scaling of heat exchangers[1–8]. A polarographic study of chromate in cooling water would, therefore, be of considerable interest.

Kolthoff and Lingane[9] studied the polarographic reduction of chromate ion in 0.1 N to 1 N sodium hydroxide, unbuffered potassium chloride, ammonium chloride-ammonia buffer at pH 8-9 and dimethyl ammonium chloride-diethyl amine at pH 10, as supporting electrolytes and studied various reduction steps. Urone[10] applied the single wave of chromate in sodium hydroxide obtained by Kolthoff and Lingane[9] to a micro-procedure for the determination of chromium in dusts and mists.

Irregular polarograms[11] with $E_{1/2}$,-0.26 and -1.1V Vs SCE of chromate were obtained from 0.5 M sodium fluoride and 0.01 per cent gelatine as base electrolyte. Shapes depend upon the pH of the solutions.

Tondeur and coworkers[12] elucidated the reaction mechanism and studied the influence of supporting electrolytes on the reduction of chromates. Dolezal[14] et al studied the polarographic behaviour of chromates in amino alcohols.

The mechanism of reduction of chromate ions was also studied by Budevski and coworkers[13]. They showed that it proceeds through the three stages: Cr^{6+}—Cr^{3+}—Cr^{2+} —Cr.

The present investigation was undertaken to carry out polarographic studies on the reduction of chromate in cooling water under various conditions and to evolve a polarographic method for the determination of chromate.

Experimental

All the polarograms were recorded on a LP-60 self-recording polarograph. A fine capillary with characteristic $m^{2/3}\ t^{1/6} = 2.89$ was used. All studies were carried out in H type Novek cell of 20 ml. capacity. The second arm of the cell was isolated by a sintered disc and agar bridge. The circuit consisted of a saturated calomel electrode (S.C.E.) as reference, agar bridge and a dropping mercury electrode. Nitrogen was bubbled through the cell for 15 min. to effect deaeration before each experiment. Analytical grade mercury was used in a dropping electrode. All the polarographic studies were carried out at 25°C. All the chemicals used were of A.R. quality.

Stock solutions of chromate were prepared by dissolving potassium chromate in water. The solutions were standardized against sodium thiosulphate iodometrically[15]. 0.1 N solution of sodium sulphate was used as supporting electrolyte. 0.01 per cent solution of gelatine was used as maximum suppressor.

Cooling water samples were collected from the miscellaneous service cooling tower in the gas reforming plant at Sindri. Typical concentration of some important constituents in the water and the pH are given in Table 1.

TABLE 1—CHEMICAL CHARACTERISTICS OF THE COOLING WATER

(pH 6.5—7.0)

Constituents	Concentration, ppm
1. Ammoniacal nitrogen	80
2. Total nitrite+nitrate nitrogen	52
3. Chloride	20
4. SO_3	70
5. Calcium	40

A synthetic water with the above composition (Table 1) was prepared by adding calculated amount of ammonium nitrate, sodium chloride, ammonium bicarbonate and calcium sulphate to distilled water The following sets of experiments were performed to study the polarographic behaviour of chromate under various conditions.

(i) *Polarography of Chromate in Distilled Water*: 50 ml. of 0.34 millimolar solution of potassium chromate in distilled water was taken in a 100 ml. volumetric flask to which was added 10 ml. of 1.0 M sodium sulphate and 10 ml. of 0.1 per cent gelatine solution. The solution was then made upto 100 ml. and 15 ml. of this solution was taken in the polarographic H cell. Nitrogen was bubbled and a polarogram was recorded (Fig. 1, Curve A).

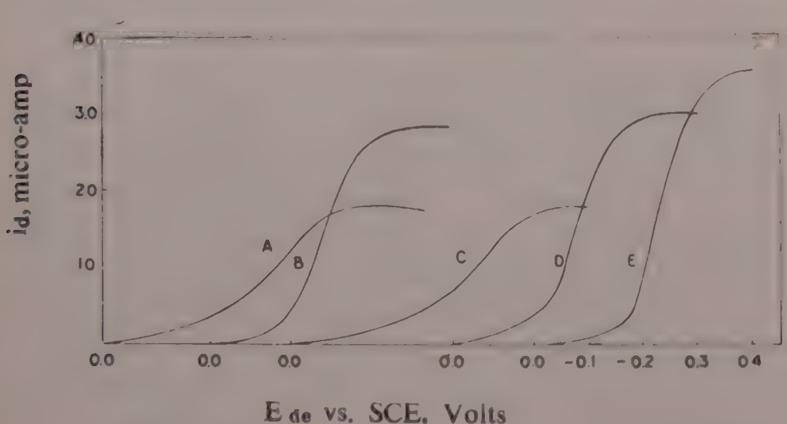

Fig. 1—Polarographic Behaviour of CrO_4^{2-} in Distilled & Synthetic Water.

(A) Polarogram of 0.17 milli-molar CrO_4^{2-} + 0.1 M Na_2SO_4 + .01% gelatine in distilled water.

(B) Polarogram of 0.17 milli-molar CrO_4^{2-} + 0.1 M Na_2SO_4 + .01% gelatine in synthetic water.

(C) Polarogram of 0.17 milli-molar CrO_4^{2-} + 0.1 M Na_2SO_4 + .01% gelatine + 10 ppm sodium polyphosphate in distilled water.

(D) Polarogram of 0.17 milli-molar CrO_4^{2-} + 0.1 M Na_2SO_4 + .01% gelatine + 10 ppm sodium polyphosphate in synthetic water.

(E) Polarogram of 50 ml. of cooling water in 0.1 M Na_2SO_4 + .01% gelatine.

[Note: All polarograms started from −0.0 applied potential.]

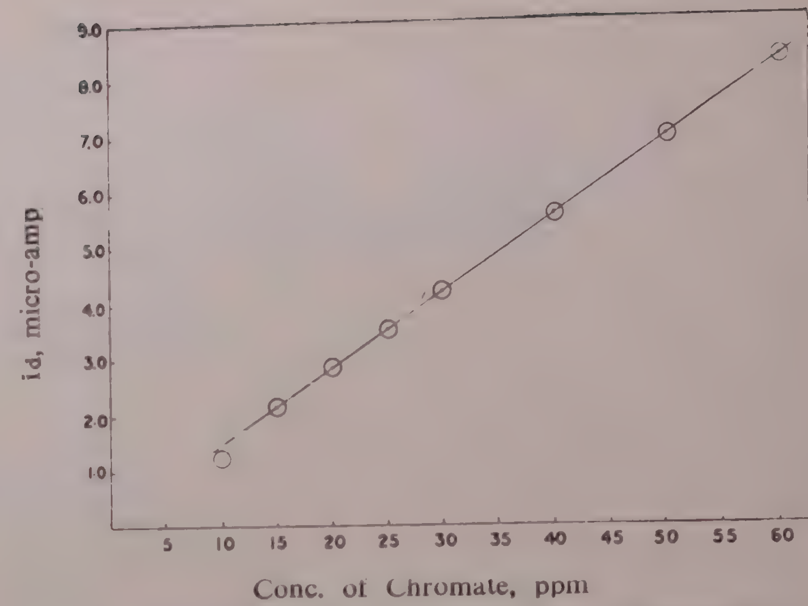

Fig. 2—Plot of Diffusion Current (i_d) vs. Concentration of CrO_4^{2-}.

(ii) *Polarography of Chromate in Synthetic Water*: 50 ml. of 0.34 millimolar solution of potassium chromate in synthetic water was taken in a 100 ml. volumetric flask, to which was added 10 ml. of 1.0 M sodium sulphate and 10 ml. of 0.1 per cent gelatine. The solution was then made up to 100 ml. and 15 ml. of it was taken and a polarogram was recorded (Fig. 1, Curve B).

(iii) *Polarography of Chromate in Distilled and Synthetic Waters in presence of Sodium Polyphosphate*: Experiments as in (i) and (ii) were performed in presence of 20 ppm sodium polyphosphate for studying its effect on the polarographic reduction of chromate (Fig. 1, Curves C & D).

(iv) *Dependence of i_d on Chromate Concentration*: 50 ml. of the solutions containing different decreasing amounts of chromate in synthetic water with 20 ppm of sodium polyphosphate were taken in a series of 100 ml. volumetric flask. 10 ml. of 1.0 M sodium sulphate and 10 ml. of 0.1 per cent gelatine were then added. The solutions were then made up to 100 ml. and 15 ml. of the solution was taken in the polarographic cell and polarograms were recorded for each concentration of chromate. From these polarograms the values of i_d were found out (Table 3) and plotted against the concentration of chromate. A standard curve for chromate was obtained (Fig. 2).

(v) *Chromate in Cooling Tower Water*: 50 ml. of the cooling tower water containing chromate and polyphosphate was taken in 100 ml. volumetric flask and 10 ml. of 1.0 M sodium sulphate and 10 ml. of 0.1 per cent gelatine solution were next added and the solution made up to 100 ml. In polarographic H cell, 15 ml. of this solution was taken, deaerated for 15 min. and a

TABLE 2—VALUES OF $E_{1/2}$, i_d, I AND n FOR CHROMATE UNDER VAROIUS CONDITIONS

Supporting Electrolyte & Medium	$E_{1/2}$ Vs SCE, volts	i_d, micro-amp	$I = \frac{i_d}{Cm^{2/3} t^{1/6}}$ Diffusion Current Constant	n From Ilkovic Equation
(a) 0.17 millimoler CrO_4^{2-} +0.1M Na_2SO_4+0.01% gelatine in distilled water	−0.30 volts	1.8	3.66	2
(b) 0.17 millimoler CrO_4^{2-} +0.1M Na_2SO_4+ 0.01 % gelatine in Synthetic water	−0.22 volts	3.0	5.97	3
(c) 0.17 millimole CrO_4^{2-} +0.1M Na_2SO_4+10 mg/l sodium polyphosphate +0.01% gelatine in distilled water.	−0.32 volts	1.8	3.66	2
(d) 0.17 millimole CrO_4^{2-} +0.1M Na_2SO_4+10 mg/l sodium polyphosphate +.01% gelatine in synthetic water	−0.22 volts	3.0	5.97	3
(e) 50 ml. of cooling water in 0.1M Na_2SO_4+.01% gelatine	−0.23 volts	3.6	—	—

TABLE 3—DEPENDENCE OF DIFFUSION CURRENT (i_d) ON THE CONCENTRATION OF CHROMATE

Supporting Electrolyte — *0.1M Na_2SO_4*
Maxima Suppressor — *0.01% Gelatine*

Conc. of Chromate, in millimole/1	Conc. of Chromate, mg/l.	$E_{1/2}$ Vs SCE, volts	i_d Diffusion Current, micro-amp	I, Diffusion Current Constant
0.51	60	−0.24	8.3	5.52
0.42	50	−0.24	6.9	5.70
0.34	40	−0.235	5.6	5.70
0.25	30	−0.23	4.2	5.81
0.21	25	−0.23	3.5	5.77
0.17	20	−0.23	2.85	5.80
0.125	15	−0.22	2.1	5.84
0.085	10	−0.22	1.2	5.83
			Average	5.75

TABLE 4—DETERMINATION OF CHROMATE IN COOLING WATER SAMPLES

(50 *ml. of cooling water sample with* 0.1*M sodium sulphate and* .01% *gelatine*)

Water Sample No.	Chromate by Iodometry, mg./l.	i_d Diffusion Current, micro-amp.	Chromate by Polarography, mg./l.	Standard Deviation
1	27.0	2.0	26.0	1.82
2	49.5	3.6	49.6	0.86
3	27.0	2.1	27.0	0.86
4	17.4	1.5	17.25	0.50
5	36.8	2.8	37.80	1.40
6	57.2	4.2	58.6	1.85
7	36.8	2.8	37.6	1.06
8	31.0	2.4	31.6	0.86
9	45.5	3.4	46.5	1.70
10	54.3	4.0	55.0	1.52

polarogram was recorded at a suitable sensitivity (Fig. 1, Curve E). Diffusion current was found out and compared with the standard curve (Fig. 2). These results were compared with standard iodometric method[15], and a standard deviation was calculated (Table 4).

Results and Discussion

It is clear (Fig. 1, Curve A) that chromate with 0.1 M sodium sulphate and 0.01 per cent gelatine gives a single wave with $E_{1/2}$ = −0.30 Vs SCE, which is most suitable for studying the polarographic behaviour of chromate under various conditions in the cooling tower water. The comparison of curves A & B (Fig. 1) reveals that the wave in synthetic water (Curve B) is well defined with diffusion current higher than that obtained in distilled water (Curve A). The value of $E_{1/2}$ has also changed to −0.22 V Vs S.C.E. in synthetic water, due to the presence of extra amounts of salts. The nature of the polarographic wave depends on the concentration of supporting electrolyte[16]. Polarograms (Fig. 1, Curves C & D), obtained in presence of sodium polyphosphate (PO_4=10 ppm) are similar to those obtained without polyphosphate (Fig. 2, Curves A & B). Hence polyphosphate does not have any effect on the polarography of chromate at this concentration range.

The values of $E_{1/2}$, i_d, I and n calculated for chromate in sodium sulphate as supporting electrolyte are given in Table 2.

As the plot of log $\frac{i}{i_d - i}$ against E_{de} for each curve of Fig. 1, gave a slope higher than 0.054, the systems have been found to be irreversible. The value of n was calculated from the Ilkovic equation:

$$i_d = 605\ nCD^{1/2}\ m^{2/3}\ t^{1/6}. \qquad \ldots(1)$$

The value of Diffusion Coefficient, D, was obtained from conductivity of chromate at infinite dilution which has been given as $1.07 \times 10^{-5}/Cm^2/sec^{-1}$ at 25°C by Kolthoff and Lingane[9]. By applying appropriate values of i_d, C, D, $m^{2/3}$ $t^{1/6}$ to equation (1) the values of n were calculated (Table 2) and found to be 2 in case of experiments performed in distilled water and 3 in synthetic water. From these values of n, it is clear that with 0.1 M, sodium sulphate as supporting electrolyte Cr^{6+} is reduced to Cr^{2+} in distilled water and to Cr^{3+} in synthetic water.

The results given in Table 3 show that the values of i_d obtained from polarograms are quite dependent upon the concentrations of chromate. The plot of i_d against the concentration of chromate is found to be linear (Fig. 2) and is used as the standard for the determination of chromate in cooling water. It is also clear that the $E_{1/2}$ and diffusion current constants for chromate in sodium sulphate as supporting electrolyte are constant up to 0.51 M concentration.

Polarographically chromate in cooling tower water can be determined by two methods viz. (1) The step height—concentration plot method[17] and (2) Absolute method[18] i.e. the use of diffusion current constant. In the cooling tower water, the concentration of chromate was found out by obtaining the polarogram of an unknown sample. The diffusion current was calculated and corresponding chromate concentration was found out from calibration graph (Fig. 2). The results of analyses of various cooling tower waters were further compared with those obtained by standard iodometric method and standard deviation was calculated (Table 4). The polarographic method developed is simple, quick and can be applied in the routine analysis of chromate in cooling waters.

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Investigation into the Use of Algae for Removing Ammonium Nitrogen from Nitrogenous Industrial Wastes Part I—Laboratory Batch Studies

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The use of algae for removing ammonium nitrogen from nitrogenous industrial wastes containing many times more nitrogen than sewage, has been studied in the laboratory using synthetic effluents without controlling temperature, incident day light intensity and pure culture conditions, thus simulating outdoor environmental conditions. These investigations have shown that wherever high ammonium nitrogen is the chief polluting constituent in an effluent biological treatment by algae might be the answer. This algal treatment would not only remove from waste waters the high amount of nitrogen which causes so much pollution problems but also provides a distinct possibility of recovering this costly plant nutrient as highly proteinaceous algal cells by developing suitable harvesting procedure.

Ammonium nitrogen in effluents discharged from ammonia manufacturing or processing industries has in recent times posed a serious water pollution problem. A stream or lake containing more than 1.2 mg/1. of ammonium nitrogen is considered unsuitable for pisciculture[1], while nitrate nitrogen, the final oxidized product of ammonium nitrogen, above a level of 10 mg./1. in a water may prove to be a potential hazard to livestocks and human beings[2–6] specially children. Ammonium nitrogen is also responsible for stimulation of excessive production of various types of nuisance aquatic organisms[7-9].

The FCI, manufacturing various types of nitrogenous fertilizers, had to face the stupendous problem of disposal of its nitrogenous effluents at Sindri. The present investigations were carried out with a view to finding out some suitable methods of treatment for nitrogenous industrial wastes in general and particularly those obtained from a nitrogenous fertilizer industry.

Literature Survey

It is known that ammonium nitrogen from sewage effluent may be removed either by chemical or biological methods[11-13]. Chemical methods like ion-exchange in columns and air-stripping in packed towers, have been studied[17, 18], but owing to the voluminous quantity and special characteristics of such an effluent, the chemical methods are not economically feasible.

Of the biological methods, the two principal processes developed are the modified activated sludge process[13–16] and removal by algae in ponds[10, 11, 19]. In the former process, the first step is the conversion of ammonium nitrogen to nitrite and finally to nitrate by vigorous aeration in the presence of aerobic activated sludge micro-organisms. The second step lies in converting this nitrate to nitrogen under anaerobic conditions by the activities of denitrifying bacteria.

In the pond process, use is made of the algal capacity of extracting nutrients from an ecosystem. Algae,

growing in such a pond, utilize the ammonium nitrogen of the waste substrate to form cell tissues. Very little of the nutrient is lost but is removed and concentrated in the algal cells.

Of the two biological processes, the modified activated sludge process appears to be the most effective biological system in terms of nitrogen removal rate, as the growth rate of the activated sludge micro-organisms are much higher than that of algae. But this process suffers from two principal limitations, the first being the heterotrophic nature of these micro-organisms which can utilize organic carbon in which a nitrogenous industrial waste is generally deficient, and in most situations supplying adequate organic carbon is very costly. Secondly, the ammonium nitrogen that is removed cannot be recovered.

In contrast, the algal process does not suffer from these limitations as algae can utilize inorganic carbon dioxide autotrophically or may utilize organic carbon with the help of heterotrophic bacteria. So viewed in terms of nutritional requirements and harvesting possibilities, it appears to offer the most easily exploited biological system. But so far utilization of algae for treatment of industrial wastes containing many times more ammonium nitrogen than sewage appear to have received little attention. Hence, a study was undertaken on the use of algae for removing ammonium nitrogen from nitrogenous industrial wastes containing high concentration of ammonium nitrogen. During this investigation a number of basic concepts came under study.

This paper presents some of the more significant findings on the usable algal cultures, algal growth and nutrients utilization in media containing various concentrations of ammonium nitrogen and in different ammonium salts, nutritional requirements for algal growth in nitrogenous effluents and harvesting of algae by autoflocculation. Being highly deficient with respect to carbon, the nitrogenous effluents (Table 1) would not provide a nutritionally balanced feed medium for algal growth. So the first requisite for biological treatability would be carbon supplementation. As the effluents contained some phenols and cyanides, it was felt that the study be first continued on synthetic nitrogenous effluents free from any toxic constituent.

TABLE 1—A TYPICAL ANALYSIS OF A NITROGENOUS FERTILIZER FACTORY EFFLUENT

Characteristics	Concentration
pH	8.5
Alkalinity as $CaCO_3$	860 mg/l
Hardness as $CaCO_3$	100 ,,
Sulphate as SO_4	1000 ,,
Ammonium nitrogen	400 ,,
Oxidised nitrogen	25 ,,
Total Phenols	3.5 ,,
Cyanide as CN	5 ,,
Oil	20 ,,
Permanganate value (4 hrs.)	9.0 ,,
B.O.D. (5 days)	22.0 ,,
Flow	4.5 mgd (approx)

Materials and Methods

Apparatus: 3 litre glass bottles with 2.1 of synthetic effluent was used as culture vessels. A cotton plug supported the carborundum diffuser tube used for bubbling carbon dioxide through the culture. The cultures were allowed to grow under natural conditions of day-light and temperature. No attempt was made to control these physical variables in order to make the environmental conditions simulate those of an outdoor treatment plant. The daily variations of light and temperature were indicated for each set of experiments.

Feed Medium: The feed media used for these studies were synthetic nitrogenous effluents prepared by dissolving fertilizer grade ammonium sulphate in laboratory tap water with proper supplementation of alkalinity (added as calcium carbonate slurry), phosphorus (added as K_2HPO_4) and trace elements. The composition of a typical synthetic effluent is given in Table 2.

TABLE 2—COMPOSITION OF A TYPICAL SYNTHETIC NITROGENOUS EFFLUENT

Component	Concentration, mg/l
Ammonium Nitrogen	280
Phosphorus as P	17.5
Alkalinity as $CaCO_3$	356
Ca as $CaCO_3$	287
Mg as $CaCO_3$	41
Zn as $ZnSO_4.7H_2O$	2.2
Cu as $CuSO_4.5H_2O$	0.4
Co as $Co(NO_3)_2.6H_2O$	0.5
Mo as Ammonium molybdate	0.2
B as $Na_2B_4O_7.10H_2O$	9
Fe as $FeSO_4.7H_2O$	1.25
Mn as $MnSO_4.H_2O$	0.15
pH	7.1 pH Unit

Iron and manganese were fed daily as $FeSO_4.7H_2O$ (0.25 mg./1 as Fe) and Mn $SO_4.H_2O$ (0.05 mg./1. Mn) respectively to the cultures over and above their initial concentration in the feed media during the entire growth

period to avoid their chances of being precipitated out and thus becoming unavailable for algal metabolism.

Algal Seed as Inoculum: A search was made for usable algae with particular interest in large filamentous species that would provide economic harvesting possibilities. Algae, predominantly filamentous, were collected from various places, such as cooling towers of different plants, sewage, effluent drains and reservoir below the sewage and effluent outfall. These algae were cultured in the laboratory in cotton-plugged Erlenmeyer flasks using synthetic effluent as feed medium and carbon dioxide as the source of carbon. Initially it took 2-3 weeks after inoculation for the initiation of growth, but microscopic examination showed that irrespective of the nature of the initial algal inoculum, the algal population that finally developed in the cultures were predominantly *Chlorella*. This showed that the physical and chemical environments of a culture determine the type of algae that would subsequently develop despite their varied initial supply. Some other workers[20, 21] too have experienced considerable difficulty in maintaining a desirable species of algae in experimental growth units.

So no attempt was made to maintain a pure culture condition of a desirable species as it was felt that maintaining such pure culture in outdoor studies would be quite impossible as the environment would dictate the algal flora. Throughout the present studies this culture containing predominantly *Chlorella* species—subsequently identified as predominantly *Chlorella pyrenoidosa* —was used as inoculum. For its preparation, the young algae from their culture solution were centrifuged after their concentration was measured, the supernatant discarded, and the cells washed with distilled water till free of ammonium nitrogen and finally suspended in a convenient volume of double distilled water, from which a suitable aliquot was added as inoculum.

TABLE 3—AVERAGE ANALYSIS OF RAW CARBON DIOXIDE GAS

Constituents	Per cent Concentration (vol/vol)
CO_2	80
O_2	0.4
CO	1.6
H_2	10.0
CH_4	0.4
N_2 and other inert gases	7.6

Carbon Dioxide Addition and pH Control: In all these studies, except where stated otherwise, carbon dioxide having an average analysis as in Table 3 was used. pH was controlled in the level of 6.3 ± 0.3 by bubbling carbon dioxide at the approximate rate of 75 ml/litre culture/hour for eight hours during the day.

Culture Mixing: The cultures were thoroughly mixed manually four times a day while taking out samples and no continuous stirring was provided.

Procedure: To the 2 l. synthetic effluent, 60-90 mg. algae (dry weight) were added as inoculum, and carbon dioxide was bubbled slowly. The culture bottles were kept under natural daylight conditions and temperature. Growth was initiated within a few hours after inoculation, which continued till the alkalinity of culture was destroyed and the algal mass, which generally remained in suspension, flocculated and started settling. At this point, the experiment was stopped and an aliquot portion of the culture was taken out for analysis and the growth period noted. The culture was similarly analysed at the start immediately after algal inoculation. Analyses were made for optical density (E), algal suspended solid, ammonium and oxidized nitrogen, phosphate and alkalinity. Optical density was determined using test tubes of 75 mm. length and 10 mm internal diameter and 600 mμ light filter in a photoelectric colorimeter*.

Algal suspended solid was determined in terms of dry weight by centrifuging a measured aliquot from the culture solution, washing four times with distilled water in centrifuge tubes, transferring the washed algae in a small quantity of distilled water to a tared crucible and drying to a constant weight at 103°C. Analyses for ammonium nitrogen, oxidized nitrogen, phosphate and alkalinity were made on algae-free culture solution in accordance with the standard methods[22]. The difference in the initial and final analyses of the culture is a measure of the algal growth and nutrient utilization.

The dried algal mass was analysed for carbon, nitrogen, hydrogen, oxygen, ash content and phosphorus for obtaining the composition of the algal cell material.

Results and Discussion

Growth and Ammonium Nitrogen Utilization by Algae in nitrogenous effluents: For this study, the growth medium used was a synthetic nitrogenous effluent having an ammonium nitrogen content of 116 mg./1,

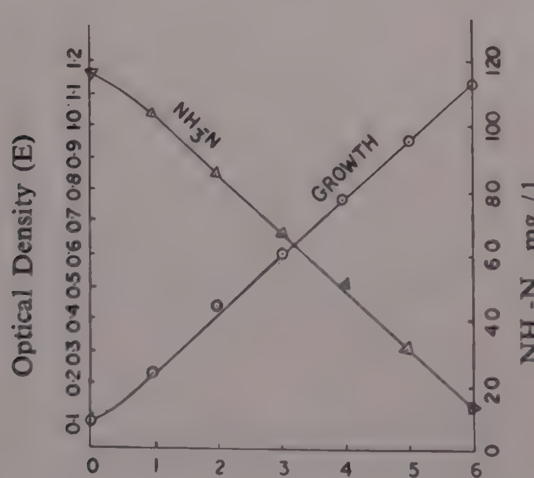
* Gallenkamp make.

the other characteristics of the medium remaining the same as those given in Table 2. The culturing conditions were: culture depth, 12.5 cm; incident day-light intensity 200-7000 ft. candles, day-time average being 3076 ft. candles approximately; temperature, 22-30°C and pH 6.3±0.3.

Algal growth was followed daily by measurement of optical density of the culture which was a function of algal concentration and ammonium nitrogen utilization by colorimetric ammonia estimation of a suitable algae-free diluted portion (Fig. 1).

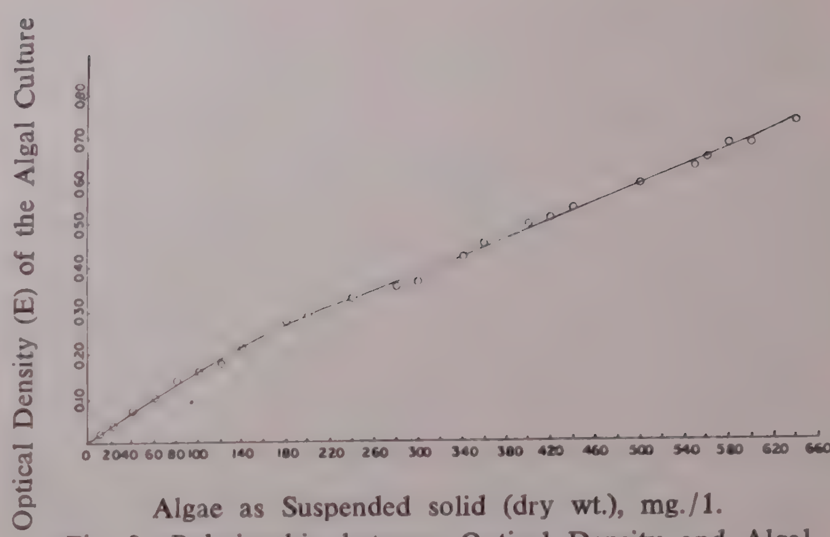
From Fig. 1, it is evident that algae can be satisfactorily cultured in a synthetic effluent containing three to four times ammonium nitrogen than sewage and that the rate of nitrogen removal, other things remaining same, is a function of the rate of cell tissue synthesis i.e., algal growth. In a growth period of 6 days, optical density increased from 0.08 to 1.13 and ammonium nitrogen decreased from 116 to 12 mg./1.

Relationship between Optical Density and Algal Suspended Solid: The culture density (i.e., the concentration of algae per unit volume) is generally evaluated in terms of cell count, dry weight and photometric measurement either as per cent transmission (% T) or as optical density (E). Dry weight measurements show large deviations when samples are small and cell count is generally much time-consuming. So it was felt that optical density measurement by photoelectric colorimeter might afford the most suitable method to follow the progress of algal growth. In as much as Beer's Law is likely to be valid only for true solution, it is surprising that it holds good for algal suspension too.



Time, days

Fig. 1—Algal Growth and Ammonium Nitrogen Utilization in Synthetic Effluent containing 116 mg./1 of Ammonium Nitrogen.



Algae as Suspended solid (dry wt.), mg./1.

Fig. 2—Relationship between Optical Density and Algal Suspended solid of a Chlorella (predominantly) Culture Growing in a Synthetic Effluent containing 280 mg./1. of NH_3 – N.

In colorimetric methods it is assumed that at the wave length selected, there is equivalence between algal concentration and optical density. For this study a stock algal suspension was first prepared by utilizing centrifuged and washed algae obtained from a known volume of an algal culture of known concentration. Aliquot portion of this was diluted to different degrees and optical density determined using 600 m μ light filter (Fig. 2).

The curve (Fig. 2) would give an approximate relationship between the optical density and the algal concentration of a predominantly *Chlorella pyrenoidosa* culture, and in all subsequent studies the algal concentration as measured by dry weight compared favourably with the values obtained by using this curve.

Algal Growth and Ammonium Nitrogen Utilization in Effluent Samples Containing Various Levels of Ammonium Nitrogen: Ammonium nitrogen levels in the synthetic effluent were varied from 100 to 500 mg./1. other characteristics remaining the same as in Table 2. The culturing conditions during this set of experiments were as follows: culture depth, 12.5 cm; incident day-light intensity, 360-11,000 ft. candles, daytime average being 4450 ft. candles, approx.; pH, 6.3±0.3; temperature, 27-35°C.

The results (Table 4) show that the rates of algal growth and ammonium nitrogen utilization have remained practically the same in all the synthetic effluents, irrespective of their ammonium nitrogen content. Even as high as 500 mg./l. of ammonium nitrogen in an effluent did not exert any inhibitory effect on algal growth and nitrogen metabolism.

Algal Growth and Ammonium Nitrogen Utilization in Effluent Samples Containing Different Ammonium Salts: A set of algal growth and ammonium nitrogen utilization experiments were performed with synthetic effluents containing different ammonium salts, the levels of ammonium nitrogen and other macro and micronutrients remaining the same as in Table 2. For this study, three ammonium salts, viz. ammonium chloride, ammonium nitrate and ammonium bicarbonate, were selected as sources of ammonium nitrogen. The algal growth and ammonium nitrogen utilization in media containing these salts were compared with that containing ammonium sulphate. The culturing conditions were: culture depth, 12.5 cm; incident day-light intensity, 360-10,000 ft. candles, day time average being 4100 ft. candles approximately; pH, 6.5 ± 0.5 and temperature, 26-30°C (Table 5).

The results show that the rate of ammonium nitrogen utilization by algae in effluents containing ammonium chloride, ammonium bicarbonate and ammonium sulphate was more or less similar, but this rate was somewhat lower in the effluent containing ammonium nitrate.

The growth rate seemed to be highest (167 mg./1./day) in the effluent sample containing ammonium bicarbonate and lowest (116 mg./1./day) in that containing ammonium nitrate.

Algal Growth and Ammonium Nitrogen Utilization in Effluents Samples with Alkalinity Supplied From Different Chemicals: Several workers[23] (on sewage effluent) have shown that the alkalinity of pond waters decreased as the algal concentration in the pond increased, which had been often explained by the following acid-forming reaction[24].

$$1.0\ (NH_4^+) + 5.7\ (CO_2) + 3.4\ (H_2O) \rightarrow C_{5\cdot7}\ H_{9\cdot8}\ O_{2\cdot3}\ N_{1\cdot0} + 6.25\ O_2 + 1H^+$$

In other words, when an ammonium salt is the nitrogen source for algae, the consumption of 1M of ammonium salt is accompanied by the production of 1M of hydrogen ion.

It was also observed during the present investigation that ammonium nitrogen uptake by algae was always associated with alkalinity destruction, and that for each part of ammonium nitrogen utilized about 3.2-3.4 parts of alkalinity was destroyed, the theoretical relationship being 3.57 parts alkalinity destruction for each part ammonium nitrogen utilization. It accrues, therefore, that for stripping ammonium nitrogen from a waste water by algae, there should either be a suitable amount of alkalinity in the effluent itself, or the same should be supplemented, to neutralize the acid formed by ammonium nitrogen metabolism of algae, otherwise pH of the growth medium would soon become too low to support algal growth.

A study was therefore, undertaken to see whether the nature of the alkaline chemical would play any part in retarding or enhancing algal growth vis-a-vis ammonium nitrogen utilization in a growth medium. Three commonly used alkaline chemicals viz. calcium carbonate, lime and soda ash, were used as sources of alkalinity, other characteristics of the medium remaining the same as the synthetic effluent of Table 2. The culturing conditions were: culture depth 12.5 cm; incident daylight intensity 200 to 10,000 ft. candles, day time average being 4000 ft. candles approximately; pH, 6.3 ± 0.3 and temperature, 32-42°C.

The results (Table 6) show that the average rates of algal growth and ammonium nitrogen uptake are practically independent of the nature of the alkaline chemical present. For a desired degree of the algal growth and ammonium nitrogen utilization, a medium must contain a certain amount of alkalinity for which any of the three chemicals studied may be used. Where no alkalinity was supplemented, growth practically ceased after 3.5 days when all the natural alkalinity of the medium was exhausted, whereas in the cultures where sufficient alkalinity was present growth continued till the seventh day after inoculation.

Algal Growth and Ammonium Nitrogen Utilization in Effluents Samples With and Without Trace Elements Supplementation: The deficiency of trace elements, like iron, manganese, zinc, copper, cobalt, molybdenum, boron, etc., in a medium would adversely affect the algal growth and nutrient utilization. These elements are generally present in the natural surface and waste waters. But on occasions some of these may become unavailable to algae by being precipitated out as their highly insoluble oxides or hydroxides. In laboratory cultures, trace elements are generally supplemented, though this may not be always necessary as these elements may ingress either from the tap water or impurities from chemicals. This study on trace element supplementation was made with a view to finding out how far tap water and chemicals used in media making could meet the trace element requirement of a dense algal culture and to what extent algal growth is affected by them.

In this study, the growth media used were ammonium sulphate solution in tap water with ammonium nitrogen level 280 mg./1. plus 17.5 mg./1. of phosphate phosphorus (added as K_2HPO_4) plus adequate alkalinity, in one case as $CaCO_3$ BP quality (growth medium 1)

TABLE 4—ALGAL GROWTH AND AMMONIUM NITROGEN UTILIZATION IN SYNTHETIC EFFLUENTS CONTAINING DIFFERENT LEVELS OF AMMONIUM NITROGEN

(Average of Duplicate Samples)

Growth Medium (Synthetic Effluent Sample) No.	Ammonium Nitrogen Level in the Effluent Sample	Initial Analysis of Cultures						Growth Period, days	Final Analysis of Cultures after Stipulated Growth Period							Average Rate of Algal Growth, mg/l/day	Average Rate of Ammonium Nitrogen utilization, mg/l/day
		Optical Density, E	Algae as Suspended Solid, mg/l	Inorg. Nitrogen, mg/l: Ammonium Nitrogen	Inorg. Nitrogen, mg/l: Oxidized Nitrogen	Phosphate as P, mg/l	Alkalinity as $CaCO_3$, mg/l		Optical Density, E	Algae as Suspended Solid, mg/l	Inorg. Nitrogen, mg/l: Ammonium Nitrogen	Inorg. Nitrogen, mg/l: Oxidized Nitrogen	Phosphate as P, mg/l	Alkalinity as $CaCO_3$, mg/l	Acidity as $CaCO_3$, mg/l		
1	100	0.10	70	100	5	17.5	356	7	1.10	1090	2	4	3.5	20	0.0	145	14
2	200	0.10	70	200	7	17.5	356	7	1.13	1146	92	7	3.4	10	0.0	154	15
3	300	0.10	70	300	9	17.5	356	7	1.10	1170	187	9	3.4	0.	2.0	157	16
4	400	0.10	70	400	10	17.5	356	7	1.16	1170	286	10	3.5	0.0	2.0	157	16
5	500	0.10	70	500	10	17.5	356	7	1.22	1160	387	10	3.3	0.00	4.0	156	16

TABLE 5—ALGAL GROWTH AND AMMONIUM NITROGEN UTILIZATION IN SYNTHETIC EFFLUENTS CONTAINING VARIOUS AMMONIUM SALTS AS SOURCES OF AMMONIUM NITROGEN

(Average of Duplicate Samples)

Growth Medium (Synthetic Effluent Sample) No.	Source of Ammonium Nitrogen in the Effluent	Initial Analysis of Cultures						Growth Period, days	Final Analysis of Cultures after Stipulated Growth Period							Average Rate of Algal Growth, mg/l/day	Average Rate of Ammonium Nitrogen utilization, mg/l/day
		Optical Density, E	Algae as Suspended Solid, mg/l	Inorg-Nitrogen, mg/l: Ammonium Nitrogen	Inorg-Nitrogen, mg/l: Oxidized Nitrogen	Phosphate as P, mg/l	Alkalinity as $CaCO_3$, mg/l		Optical Density, E	Algae as Suspended Solid, mg/l	Inorg-Nigrogen, mg/l: Ammonium Nitrogen	Inorg-Nigrogen, mg/l: Oxidized Nitrogen	Phosphate as P, mg/l	Alkalinity as $CaCO_3$, mg/l	Acidity as $CaCO_3$, mg/l		
1	Ammonium Chloride	0.15	90	280	10	17.5	356	7	1.21	1165	172	10	3.5	0.0	16	154	15
*2	Ammonium Bicarbonate	0.15	90	280	12	17.5	1080	7	1.30	1256	170	12	3.0	600	0.0	167	16
3	Ammonium Nitrate	0.15	90	280	280	17.2	356	7	1.06	899	197	278	3.8	72	0.0	116	12
4	Ammonium Sulphate	0.15	90	280	10	17.5	356	7	1.18	1221	169	10	3.2	0.0	2.0	162	16

*In growth medium 2, no alkalinity was supplemented from external source as alkalinity from ammonium bicarbonate was sufficiently high.

TABLE 6—ALGAL GROWTH AND AMMONIUM NITROGEN UTILIZATION IN SYNTHETIC EFFLUENTS CONTAINING DIFFERENT SOURCES OF ALKALINITY
(Average of Duplicate Samples)

Growth Medium (Synthetic Effluent Sample) No.	Source of Alkalinity in Growth the Medium	Initial Analysis of Cultures: Optical Density, E	Initial: Algae as Suspended Solid, mg/l	Initial: Inorg. Nitrogen, mg/l: Ammonium Nitrogen	Initial: Inorg. Nitrogen, mg/l: Oxidized Nitrogen	Initial: Phosphate as P, mg/l	Initial: Alkalinity as $CaCO_3$, mg/l	Growth Period, days	Final Analysis of Cultures after Stipulated Growth Period: Optical Density, E	Final: Algae as Suspended Solid, mg/l	Final: Inorg. Nitrogen, mg/l: Ammonium Nitrogen	Final: Inorg. Nitrogen, mg/l: Oxidized Nitrogen	Final: Phosphate as P, mg/l	Final: Alkalinity as $CaCO_3$, mg/l	Final: Acidity as $CaCO_3$, mg/l	Average Rate of Algal Growth, mg/l/day	Average Rate of Ammonium Nitrogen utilization, mg/l/day
1	Tap water plus the Alkalinity associated with $K_2H\ PO_4$. No extra alkali was added	0.09	63	280	10	17.5	126	3.5	0.64	638	225	10	12.5	0.0	32	164	16
2	Calcium carbonate	0.09	63	280	10	17.5	312	6	1.05	1040	187	10	3.6	22	0.0	163	16
3	Sodium carbonate	0.09	63	280	10	17.5	332	6	1.04	1020	187	10	4.1	30	0.0	160	16
4	Lime	0.09	63	280	10	17.5	310	6	1.05	1040	186	10	3.5	24	0.0	163	16

TABLE 7—ALGAL GROWTH AND AMMONIUM NITROGEN UTILIZATION IN SYNTHETIC EFFLUENTS WITH AND WITHOUT TRACE ELEMENTS SUPPLEMENTATION
(Average of Duplicate Samples)

Growth Medium (Synthetic effluent) No.	Source of Alkalinity Supplementation in the Effluent	Amount of trace Elements Supplementation	Initial Analysis of Cultures: Optical Density, E	Initial: Algae as Suspended Solid, mg/l	Initial: Inorg. Nitrogen (mg/l): Ammonium Nitrogen	Initial: Inorg. Nitrogen (mg/l): Oxidised Nitrogen	Initial: Phosphate as P, mg/l	Initial: Alkalinity as $CaCO_3$, mg/l	Growth Period, days	Final Analysis of Cultures after Stipulated Growth Period: Optical Density, E	Final: Algae as Suspended Solid, mg/l	Final: Inorg. Nitrogen, mg/l: Ammonium Nitrogen	Final: Inorg. Nitrogen, mg/l: Oxidised Nitrogen	Final: Phosphate as P, mg/l	Final: Alkalinity as $CaCO_3$, mg/l	Final: Acidity as $CaCO_3$, mg/l	Average Rate of Algal Growth, mg/l/day	Average Rate of Ammonium Nitrogen utilization, mg/l/day
1	Powdered Calcium carbonate BP-200 mesh	0.0	0.05	44	280	10	17.5	356	8	0.90	940	190	10	3.5	72	0.0	113	11
1a	-do-	Only Fe & Mn was supplemented. Fe-0.25 mg/l/day; Mn-0.05 mg/l/day	0.05	44	280	10	17.5	356	8	1.00	1100	175	10	3.0	38	0.0	132	13
2	Powdered marble chips BS-200 mesh	0.0	0.05	44	280	10	18.0	356	8	0.93	1000	181	10	3.4	40	0.0	119	12
2a	-do-	Only Fe & Mn was supplemented Fe-0.25 mg/l/day; Mn-0.05 mg/l./day	0.05	44	280	10	17.8	356	7	1.04	1165	171	9	3.0	28	0.0	160	16

and in another case as powdered marble chips (growth medium 2), both of —200 mesh (B.S.S.) size.

The growth medium 1 was taken in duplicate bottles (2.1 sample in a 3 1. bottle), 1 and 1a. In bottle 1, no trace element was supplemented whereas in la only iron and manganese were supplemented daily as usual. Similar treatment was given to growth medium 2. In bottle 2, no trace element was supplemented and in 2a only iron and manganese supplementation was made daily.

The culturing conditions were: culture depth, 12.5 cm; pH, 6.3±0.3; incident day-light intensity, 200-7000 ft. candles, day-time average being 3076 ft. candles approximately; and temperature., 23-37°C. The results (Table 7) show that trace element requirement of a dense algal culture is partially met from tapwater and from impurities associated with chemicals. With powdered marble chips algal growth and nutrient utilization were better than those of calcium carbonate BP quality, confirming that the former with more impurities supplies more trace element to the medium. But growth was definitely higher when iron and manganese were supplemented in the media.

Algal Growth and Ammonium Nitrogen Utilization in Effluent Samples Containing Different Sources of Phosphate Phosphorus: Phosphorus is present in algal cell material[7], and accounts for about 1 per cent of its dry weight. So to make an waste water containing ammonium nitrogen amenable to algal treatment, it must be supplemented by a suitable amount of phosphorus. A study was, therefore, made on the algal growth and ammonium nitrogen uptake in media containing different sources of phosphate phosphorus. The phosphates studied were potassium phosphate ($K_2H\ PO_4$), sodium phosphate ($Na_3\ PO_4.12.H_2O$ and calcium superphosphate (water-soluble portion).

The synthetic effluents studied were almost identical in every respect used earlier (Table 2) except for the source of phosphate. The culturing conditions were: culture depth, 12.5 cm; incident day-light intensity, 200 to 10,000 ft. candles, day time average being 4450 ft. candles approximately; pH, 6.3±0.3 and temperature, 30-42°C.

The results (Table 8) show that the rates of algal growth and ammonium nitrogen utilization were highest (growth rate 171 mg./1/day and nitrogen utilization rate 16.8 mg./1/day) in medium 2 containing K_2HPO_4. These rates were lowest in medium 1 where no phosphorus was supplemented except that which ingressed the medium with algal inoculum. The growth and ammonium nitrogen utilization with sodium phosphate and calcium superphosphate water extract were almost identical but appreciably lower than those obtained with potassium phosphate.

It may be observed (Fig. 3) that algal growth has slowed down in medium 1—containing zero phosphate supplementation—after one day and practically ceased after 3 days. In both the media 3 and 4—containing sodium ortho-phosphate and calcium superphosphate water extracts respectively—growth slowed down after 3 days and practically ceased after 4 days. But in medium 2—containing potassium phosphate—growth rate was uniformly high. Growth inhibition in medium 1 was certainly due to phosphate deficiency but phosphate was not limiting in media 3 and 4 (vide Table 8). Naturally retarded algal growth in media 3 and 4 should be ascribed to some other factors, and it seems that potassium deficiency in these media (as no potassium was included) probably played the decisive role in growth inhibition.

Algal Growth and Ammonium Nitrogen Utilization in Effluent Samples with Different Concentrations of Carbon Dioxide: Some workers[25] have observed that higher concentrations of carbon dioxide sometimes proves toxic to algae, although others have used as high as 100 per cent of the gas. It has already been shown that due to the ready availability of 80 per cent carbon dioxide in this laboratory, all the experiments have been performed with the same carbon dioxide gas. But to ascertain if algal growth rate and nitrogen utilization are improved by using diluted gas, a number of experiments were performed with 20 per cent carbon dioxide, using the same synthetic effluent as that of Table 2.

In one set of duplicate bottles (2 1. effluent in a 3 1. bottle) 80 per cent carbon dioxide was bubbled at

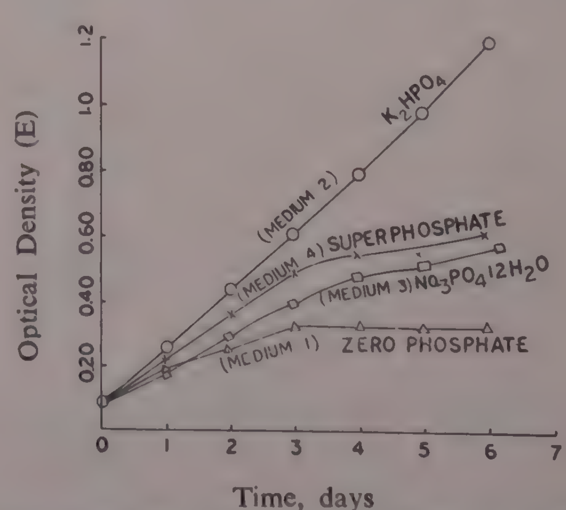


Fig. 3—Relative Growth of Algae in Synthetic Effluent containing Various Sources of Phosphate Phosphorus.

75 ml/1. medium/hr and in the second set 20 per cent gas was bubbled at the rate of 280 ml/1. medium/hr., with pH controlled in both sets at 6.3±0.3. The other culturing conditions were: culture depth, 12.5 cm; incident daylight intensity, 200-11,000 ft. candles, day-time average being 4040 ft. candles approximately; temperature, 31-41°C.

The results (Table 9) show that the average rates of algal growth and ammonium nitrogen utilization improve to appreciable extent with 20 per cent gas over those using 80 per cent.

Algal Growth and Ammonium Nitrogen Utilization in Samples with Carbon Supplementation from Different Sources: It has been shown earlier (Table 1) that a nitrogenous fertilizer factory waste is nutritionally deficient in carbon. The studies so far conducted indicated that the carbon deficiency can be made up with supplementation of carbon dioxide gas. It is also known that algae of oxidation ponds utilize the CO_2 gas generated *in situ* by bacterial decomposition of organic compounds present in them. So a study was made to assess whether organic wastes with high B.O.D., if readily available, can be utilized as a source of carbon for treatment of nitrogenous waste waters by algae using the same effluent (as in Table 2) as growth medium.

In one set of duplicate culture samples (2 1. medium in 3 1. bottles), 80 per cent carbon dioxide was bubbled as usual and in the other duplicate set glucoses (plus sewage seed) was used as the source of carbon dioxide. Glucose was added daily in four instalments and the quantum of glucose additions was increased with increase in culture density (as measured by optical density of cultures) and was based on the pH of the culture which was maintained at 6.5—7.0. The other culturing conditions were as follows: culture depth, 12.5 cm; incident daylight intensity, 200-8,000 ft. candles, day-time average being 3150 ft. candles approximately; and day temperature, 26-35°C.

The daily glucose additions were as follows: First day 300 mg; and second, third and fourth days 750, 1150 and 800 mg respectively. On the afternoon of the fourth day, culture pH in the second set came down to 3.6 associated with development of free mineral acidity, and the entire algal mass was found to have formed into large flocs which started settling distinctly. But the algae in the first set of bottles containing carbon dioxide gas supplementation attained comparable growth and flocculation only after six days. Flocculation of the algal mass was also much pronounced and more quick in cultures containing glucose. Results are given in Table 10 and Fig. 4.

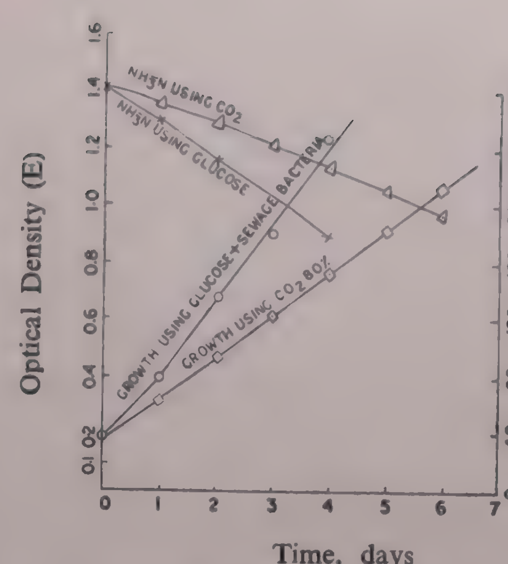


Fig. 4—Relative Growth and NH_3-N Utilization by Algae in Synthetic Effluent using Carbon from Various Sources.

The results show that the rates of algal growth and ammonium nitrogen utilization are much higher in media where carbon dioxide is generated *in situ* by the bacterial decomposition of glucose than when it is bubbled from external source. The growth rate was 250 mg/1./day with glucose and 162 mg/1./day with carbon dioxide. In the case of growth media containing glucose plus sewage bacteria as source of carbon, the ratio of ammonium nitrogen utilization to algal growth was somewhat higher indicating that micro-organisms other than algae were also active in removing some ammonium nitrogen.

Harvesting of Algae in Synthetic Effluents by Autoflocculation: During these laboratory batch studies a natural separation process was observed in most of the cases when almost the entire algal population of a culture clumped together to form big flocs which subsequently settled down to the bottom of the bottle when kept in quiescent state for a number of hours. This phenomenon happened when the alkalinity of a culture got totally exhausted giving place to a little free mineral acidity. The formation of flocs started at the pH range of 4.5-5.0 and was distinctly visible when the pH was 4.0-4.2.

Attempts to induce such autoflocculation at different stages of algal growth by lowering the alkalinity and pH of a culture to the congenial levels with acid dosing from external source were not successful. It seems algal autoflocculation takes place only during the active growth phase of a culture when by ammonium nitrogen metabolism of algae sufficient acid is produced to destory all the alkalinity of the culture medium and bring down the pH to 4.0-4.2. By controlling the initial alkalinity of a growth medium, a culture can be forced

TABLE 8—ALGAL GROWTH AND AMMONIUM NITROGEN UTILIZATION IN SYNTHETIC EFFLUENTS CONTAINING DIFFERENT SOURCES OF PHOSPHATE PHOSPHORUS
(Average of Duplicate Samples)

Growth Medium (Synthetic Effluent) Sample No.	Source of Phosphorus the Effluent	Initial Analysis of Cultures: Optical Density, E	Initial: Algae as Suspended Solid, mg/l	Initial: Inorg. Nitrogen mg/l: Ammonium Nitrogen	Initial: Inorg. Nitrogen mg/l: Oxidized Nitrogen	Initial: Phosphate as P, mg/l	Initial: Alkalinity as $CaCO_3$, mg/l	Growth Period, days	Final Analysis of Cultures after Stipulated Growth Period: Optical Density, E	Final: Algae as Suspended Solid, mg/l	Final: Inorg. Nitrogen, mg/l: Ammonium Nitrogen	Final: Inorg. Nitrogen, mg/l: Oxidized Nitrogen	Final: Phosphate as P, mg/l	Final: Alkalinity as $CaCO_3$, mg/l	Final: Acidity as $CaCO_3$, mg/l	Average Rate of Algal Growth, mg/l/day	Average Rate of Ammonium Nitrogen utilization, mg/l/day
1	No phosphate was added from external source	0.08	50	280	10	0.1	324	6	0.30	260	260	10	0.0	260	0.0	35	3
2	$K_2H\ PO_4$ (Potassium Orthophosphate, dibasic)	0.085	50	280	10	17.2	356	6	1.2	1110	179	10	3 2	0.0	0.0	176	17
3	$Na_3\ PO_4\ 12H_2O$ (Soidum Ortho phosphate, tribasic)	0.08	50	280	10	17.5	400	6	0.58	590	233	10	11.3	230	0.0	71	7
4	Clear Water extract of fertilizer grade calcium super-phosphate	0.08	50	280	10	19.5	324	6	0.62	595	230	9	12.5	140	0.0	71.5	7

TABLE 9—ALGAL GROWTH AND AMMONIUM NITROGEN UTILIZATION IN SYNTHETIC EFFLUENTS WITH VARIOUS CONCENTRATIONS OF CARBON DIOXIDE ADDITIONS
(Average of Duplicate Samples)

Experiment No.	Concentration of CO_2 gas Supplied	Initial Analysis of Cultures: Optical Density, E	Initial: Algae as Suspended Solid, mg/l	Initial: Inorg. Nitrogen, mg/l: Ammonium Nitrogen	Initial: Inorg. Nitrogen, mg/l: Oxidized Nitrogen	Initial: Phosphate as P, mg/l	Initial: Alkalinity as $CaCO_3$, mg/l	Growth Period days	Final Analysis of Cultures after Stipulated Growth Period: Optical Density, E	Final: Algae as Suspended Solid, mg/l	Final: Inorg. Nitrogen mg/l: Ammonium Nitrogen	Final: Inorg. Nitrogen mg/l: Oxidized Nitrogen	Final: Phosphate as P, mg/l	Final: Alkalinity as $CaCO_3$, mg/l	Final: Acidity as $CaCO_3$, mg/l	Average Rate of Algal Growth, mg/l/day	Average Rate of Ammonium Nitrogen utilization, mg/l/day
1	20%	0.10	70	280	10	17.5	356	5	1.2	1020	187	9	5.2	34	0.0	190	19
2	80%	0.10	70	280	10	17.5	356	5	1.04	870	199	10	7.0	64	0.0	160	16

TABLE 10—ALGAL GROWTH AND AMMONIUM NITROGEN UTILIZATION IN SYNTHETIC EFFLUENTS WITH CARBON SUPPLEMENTATION FROM DIFFERENT SOURCES
(Average of Duplicate Samples)

Experiment No.	Source of Carbon Supplementation	Initial Analysis of Cultures: Optical Density, E	Initial: Algae as Suspended Solid, mg/l	Initial: Inorg. Nitrogen, mg/l — Ammonium Nitrogen	Initial: Inorg. Nitrogen, mg/l — Oxidized Nitrogen	Initial: Phosphate as P, mg/l	Initial: Alkalinity as $CaCO_3$, mg/l	Growth Period, days	Final Analysis of Cultures after Stipulated Growth Period: Optical Density, E	Final: Algae as Suspended Solid, mg/l	Final: Inorg. Nitrogen, mg/l — Ammonium Nitrogen	Final: Inorg. Nitrogen, mg/l — Oxidized Nitrogen	Final: Phosphate as P, mg/l	Final: Alkalinity as $CaCO_3$, mg/l	Final: Acidity as $CaCO_3$, mg/l	Average Rate of Algal Growth, mg/l/day	Average Rate of Ammonium Nitrogen utilization, mg/l/day
1	CO_2 Gas (80%)	0.2	130	280	10	17.5	356	7	1.22	1261	139	10	3.0	0.0	6	162	16
2	Glucose plus sewage seed	0.2	130	280	10	17.5	356	4	1.26	1130	140	10	3.7	0.0	12	250	28

TABLE 11—AMMONIUM NITROGEN REMOVAL FROM SYNTHETIC EFFLUENT BY CONTROLLED ALGAL CULTURE USING MULTIPLE GROWTH UNITS
(Average of Duplicate Samples)

Growth Unit	Initial Analysis of the Culture: pH	Initial: Optical Density, E	Initial: Algal Solid, mg/l	Initial: Ammonium Nitrogen, mg/l	Initial: Oxidized Nitrogen, mg/l	Initial: Phosphate as P, mg/l	Initial: Alkalinity as $CaCO_3$, mg/l	Initial: Acidity as $CaCO_3$, mg/l	Growth Period, days	Final Analysis of the Culture After 7 Days of Growth Period when Almost Entire Algal Mass autoflocculated & Settled: pH	Final: Optical density, E	Final: Algal solid, mg/l	Final: Ammonium Nitrogen, mg./l	Final: Oxidized Nitrogen, mg./l.	Final: Phosphate as P, mg/l	Final: Alkalinity as $CaCO_3$, mg./l	Final: Acidity as $CaCO_3$, mg/l
Performance of the First Growth Unit	7.1	0.10	70	280	10	17.5	356	0	7	3.9	1.16	1160	170	10	3.5	0	4
Performance of the Second* Growth Unit	3.9	0.19	120	170	10	3.5 + 14	0 + 360	4	7	3.7	1.2	1120	54	10	4.0	0	20

*The feed to the second growth unit was the siphoned clear supernatant from the first growth unit after algal population in it has autoflocculated and settled to the bottom plus 14 mg/l PO_4—P(supplemented as K_2HPO) and 360 mg/l $CaCO_3$. Fe (0.25 mg/l/day) and Mn (0.05 mg/l/day) were the only trace elements added.

to auto-flocculate at any desired culture density provided other environmental conditions remain favourable for active algal growth phase. After a culture had thus autoflocculated and settled, the clear supernatant can be easily separated from the settled algal mass by decantation. Thus, from an algal culture having a density of 1000 mg./1., an algal slurry of 40,000 mg./1. concentration can be obtained by simple removal of supernatant liquor by decantation. This concentrated algal slurry can be processed further by centrifugation, drying etc.

The clear supernatant may be transferred to a new growth unit and converted into a fresh substrate for algal growth by supplementation of proper dosages of phosphate, alkalinity, trace elements and carbon etc. A dense algal culture may again be developed, and this cycle may be repeated till all the ammonium nitrogen content of the effluent comes down to a very low level. Table 11 gives the results of a typical experiment where by utilizing algal autoflocculation and settling, ammonium nitrogen level of the effluent has been brought down from 280 mg/1. to 54 mg/1. in 14 days using only two growth units. It shows that in the first growth unit, 110 mg./1. ammonium nitrogen had been removed in seven days at the expense of 1090 mg./1. algal suspended solid formation (in terms of dry weight). It also shows that the clear supernatant which was used as the feed medium to the second bottle had only 120 mg./1. algal solid remaining in suspension, i.e. about 89 per cent algal mass has been separated by autoflocculation and settling in the first growth unit. By supplementing suitable amounts of phosphate, carbon dioxide and trace elements (iron and manganese only), this supernatant was again developed into a favourable substrate for algal growth, which is evident from the final analysis of the second growth unit where 116 mg./l of ammonium nitrogen had been removed with the formation of 1060 mg./l of algal suspended solid.

Material Balance of Nutrients: In an actively growing algal culture, under ideal conditions, whatever nutrient is depleted from the liquid feed medium would be converted to algal cells, the rate of nutrient depletion depending on the composition of the cell material and the rate of algal growth. From studies so far conducted with synthetic nitrogenous effluents under various chemical and physical environments, it was observed that there existed some close relationship between nutrient (nitrogen and phosphorus) depletion and algal suspended solid formation as depletion in the levels of nutrients like nitrogen and phosphorus in a culture was always associated with a rise in the concentration of algal suspended solid. An examination of the results (Tables 4-10) would show that for the formation of about 1000 mg./l. of algal suspended solid about 100 mg./l. of nitrogen and 10-14 mg/l. of phosphorus got depleted from a culture.

From the chemical composition of dried algal cells (Table 12), it may also be seen that 9.8 parts by weight of nitrogen and 0.9 part by weight of phosphorus are present in 100 parts by weight of algae, which is in perfect agreement with nitrogen and phosphorus depletion and algal suspended solid formation data obtained from culture analysis. It accrues, therefore, that ammonium nitrogen removed from a culture was almost cent per cent converted to algal cells.

TABLE 12—AVERAGE ANALYSIS OF WASHED AND OVEN DRIED ALGAL CELLS GROWING IN SYNTHETIC EFFLUENTS

Items	Concentration, %
Carbon	52.4
Nitrogen	9.8
Hydrogen	7.4
Oxygen	27.9
Ash (including phosphorus)	2.5
Phosphorus	0.9

Phosphorus balance, of course, was not so clear as in some experiments higher depletion of phosphate phosphorus was observed than could be explained from algal yield and composition. It was probable that a little amount of phosphorus might have been precipitated during the period of high photosynthetic activity.

From the analysis of washed and oven dried algal cells (Table 12), an attempt was made to develop an empirical formula for the algal cell material. After making necessary correction for ash the percentage composition of algal cells on ash-free oven-dried basis, came to be carbon 53.4 per cent nitrogen 9.9 per cent, hydrogen 7.5 per cent, oxygen 28.3 per cent, and phosphorus 0.9 per cent, which corresponded to the following formula: $C_{148}\ H_{250}\ O_{59}\ N_{24}\ P$. The basic reaction of algal cell formation can be summarized as:

$$148\ (CO_2)\ +89\ H_2O+24\ (NH_4^+)+1(PO_4^{-3})+\text{Sun energy}= C_{148}.\ H_{250}\ O_{59}\ N_{24}\ P+165\ O_2+24H^+.$$

(alga, mol. wt. 3337)

It may be seen from this equation also that 336 parts by weight of nitrogen and 31 parts of phosphorus would be utilized during the formation of 3337 parts algal cells which is in full agreement with nitrogen, phos-

phorus and algal yield data obtained earlier from culture analyses.

Conclusion

The significant aspects of these investigations are as follows: (1) With proper supplementation of carbon, phosphorus alkalinity and trace elements an industrial waste containing as high as 500 mg./l of ammonium nitrogen can be treated with algae; (2) the average rates of algal growth and ammonium nitrogen utilization remain nearly the same irrespective of the ammonium nitrogen level of the growth medium; (3) the average rates of algal growth and ammonium nitrogen utilization are not affected by sources of ammonium nitrogen, alkalinity and phosphorus of growth media; (4) algae growing in the nitrogenous effluents were identified to be predominantly *Chlorella pyrenoidosa*, *Chlorella ellipsoidea* and *Chlorella vulgaris* being rare; (5) the pH of an algal culture could be maintained easily within the narrow range of 6.0-6.6 by controlling the feed rate of carbon dioxide when calcium carbonate/sodium carbonate was the alkaline constituent of the growth medium; (6) phosphate loss by precipitation was very small at the pH range of 6.0-6.6 and phosphate supplementation was minimum when algal cultures were allowed to grow at that pH range; (7) the average rate of ammonium nitrogen removal was roughly one-tenth of the average rate of algal growth; (8) the average rates of algal growth and ammonium nitrogen utilization were better in a medium where carbon dioxide was generated *in situ* by the bacterial decomposition of glucose than when bubbled from outside; (9) trace elements' requirement other than that of iron and manganese for a dense algal culture could only be met from tap water and impurities present in chemicals used for preparation of the growth medium; but iron and manganese needed supplementation daily; (10) agglomeration of very fine algal cells into compact masses during the active growth phase of an algal culture, the phenomenon which has often been termed as autoflocculation, was observed in almost all the cultures when their alkalinity was destroyed by the ammonium nitrogen metabolism of algae, and pH fell to 4.2 or below. This autoflocculation may be controlled by regulating the initial alkalinity of the culture medium; and (11) the clear supernatant from an autoflocculated and settled culture may be taken out by decantation and again developed into a dense algal culture after supplementing phosphate phosphorus, alkalinity, trace elements and carbon dioxide, and the cycle may be repeated till all the ammonium nitrogen of the effluent is extracted by alage.

It is expected that if a steady state condition as regards algal population, nutrient level and physical environment is maintained as is the case with continuous or semi-continuous process, the rate of algal growth vis-a-vis nitrogen removal would further improve.

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Infra Red Study of Apatite Mineral

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The nature of substitution in apatite variety of rock-phosphates of different origin has been investigated by study of their infra-red spectra using four samples. It has been suggested that the formation of carbonatoapatite occurs by replacement of fluorine or hydroxyl group by carbonate in the apatite lattice. Further, it has been concluded that all the four varieties, viz. of Jordan, Morocco, Makatea and Tunisia respectively, are mainly fluorapatite with partial formation of carbonatopatite.

Introduction

Apatite is of one of the crystalline calcium phosphates and this name has been adapted for the whole group of closely related structures. It is well-known that in the apatite lattice various types of cationic and anionic replacement can occur resulting in the formation of substituted apatite. Although the substitution of fluorine in fluorapatite—which is most abundant and widely distributed in nature—by OH^-, Cl^- and O^{2-} ions is well established, its substitution by $(CO_3)^{2-}$ ion is a controversial one. A considerable amount of effort has been devoted to the study of the apatite to explain this anomalous situation for which there exist various suggestions[1–5].

Recently, infra-red study has been applied to apatite but relatively little attention has been given to the relation between the absorption frequency and the effect of the chemical substitution, and particularly of the structural environment of the $(CO_3)^{2-}$ ion, composition and structural characteristics of the mineral.

Experimental

Materials: Synthetic hydroxy- , fluoro- and carbonato-apatites, prepared according to a method already described[6] and confirmed by x-ray and DTA methods, and representative samples of four varieties of rock phosphate—from Jordan, Tunisia, Morocco and Makatea—and one sample of limestone (Jharbeda) were used for the present investigation.

Infra-red Analysis: All the syhthetic and natural apatites and one limestone sample were studied in the solid phase by potassium bromide disc technique using the Perkin Elmer Infra-red dual grating spectrophotometer, Model 421.

Potassium bromide pellets were prepared following a nearly similar procedure described by Ingebrigtson et al.[7] In general, about 5 mg. of the sample were ground and mixed with 250 mg. of potassium bromide (reagent grade, finely ground and dried at 400°C) in an agate mortar, loaded in a die, evacuated and pressed for 10 min. at 15 tons/sq. in. pressure. The pressure was released, the die rotated by 180°, again pressed in vacuum for at least 10 min. at 20 tons pressure. The diameter of the pellet was 13 mm. having a thickness of 1 mm. The spectra was recorded from 2.5μ to 18μ using strip chart recorder and the scanning speed was 17 min.

for the full range.

Results and Discussion

The absorption curves of the four varieties of rock-phosphate, synthetic apatites and one variety of limestone are reproduced in Fig. 1 (a, b and c).

Following Romo[5] and Fischer and Ring[7], the various bands have been attributed to the various modes of vibration appropriate of the $(PO_4)^{3-}$ and $(CO_3)^{2-}$ ions. The assignments of the bands due to these ions have been made according to those given by Herzberg[8]. The wave numbers (cm^{-1}) of the absorption maxima together with their classifications and assignments are given in Table 1, which also contain the symmetry of the $(PO_4)^{3-}$ and $(CO_3)^{2-}$ groups characterizing the various apatites.

It is seen that synthetic hydroxyapatite shows three bands at 628, 602 and 563 cm^{-1} and synthetic fluorapatite three bands at 740, 602 and 575 cm^{-1} (Table 1). This difference may be used for distinguishing fluorapatite from hydroxyapatite.

Further, comparison between the infra-red absorption bands of the various apatites and other minerals given in Table 2 shows that in the natural varieties of rock-phosphate, besides fluorapatite, carbonatoapatite is also present. The appearance of the band 710 cm^{-1} in the I. R. spectrum of Jordan rock phosphate indicates the possibility of the presence of simple ionic carbonate.

Symmetry of $(PO_4)^{3-}$ *Ion:* The free $(PO_4)^{3-}$ ion has tetrahedral configuration and belongs to the point group T_d. In the ideal symmetry state only the triply degenerate vibration species, F_2, is infra-red active and therefore, the fundamental bands corresponding to ν_3 and ν_4 vibrations will be observable. Any lowering of the symmetry of the phosphate ion will be accompanied by the appearance of forbidden frequencies ν_1 and ν_2 and splitting of the degenerate modes of vibration.

According to the site group analysis for apatite[10], phosphorus atom is on a C_s site, thereby restricting the $(PO_4)^{3-}$ ion to the point group C_s, C_{2v}, C_{3v}, D_{2d} and T_d. Table 3 gives the correlation between the above point groups.

The I. R. spectra (Fig. 1) for the rock phosphate and the vibrational frequencies assigned for the phosphate ion (Table 1) show that in all the cases, there is a single absorption band for ν_1 mode, two absorption bands for ν_3 mode and excepting for three cases two absorption bands for ν_4 mode. The correlation diagram of Table 3 suggests that this result can be reasonably interpreted only on assumption that T_d symmetry of phosphate ion is lower to C_{3v}. However, this conclusion should be viewed with caution, since in some cases, the split bands may not be well resolved and if consideration is given to the possibility of unrevealed degeneracies, the molecular symmetry could be C_{2v} or C_s. In fact it has been observed that in the three cases, viz. synthetic fluorapatite, hydroxyapatite and Jordan variety of rock phosphate, ν_4 splits into three absorption bands which indicates that phosphate ion in rock phosphate equals or approaches the molecular symmetry C_{2v} or C_s. Hence, it can be concluded that the symmetry of the phosphate ion in apatite has been modified to point groups of lower symmetry and equals or approaches C_{3v}, C_{2v} or C_s but not higher symmetry.

Symmetry of $(CO_3)^{2-}$ *Ion:* The free $(CO_3)^{2-}$ ion belongs to the point group D_{3h} and generally three fundamentals are encountered, viz. ν_2, ν_3 and ν_4 in the I. R. spectrum. The site symmetry, as deduced by using site group analysis of the carbonate ion in a calcite crystal, is D_3 whereas it is C_s in aragonite. The correlation between the above point groups is given in Table 4.

The I. R. spectrum of synthetic carbonatoapatite and all the varieties of rock phosphate was compared with the calcite (Jharbeda limestone was determined as pure calcite by an earlier investigation[12]). It can be seen from the Table 2 that the frequencies observed for the $(CO_3)^{2-}$ ion and the nature of I. R. spectra, (Fig. 1) compare nearly to that of the calcite and therefore it is concluded that D_3 symmetry still holds for $(CO_3)^{2-}$ ion in the apatite although there is splitting of ν_3 band, and the reasons for which have been explained in the next section.

Structural Characteristics and Effect of Substitution: Earlier observations[13] have shown that when the ions are co-ordinated to the central metal atom, the symmetry is disturbed, and the spectrum is quite different from that expected for the free ion.

In the case of synthetic apatite as well as other varieties of rock phosphate, a lowering of symmetry of the phosphate ion has been noticed. This lowering of symmetry is expected because of the co-ordination of phosphate group to calcium atom as is evident from the crystal structure of apatite[14], in which one of the calcium atoms is co-ordinated by nine oxygen atoms and another calcium atom has sevenfold co-ordination with six oxygens of five phosphate groups in addition to the hydroxyl or fluoride ion.

In the case of $(CO_3)^{2-}$ ion, discussed earlier, there is no lowering of symmetry and it had more or less a fixed structural configuration. In the literature, one of the suggestions put forward to explain the presence of

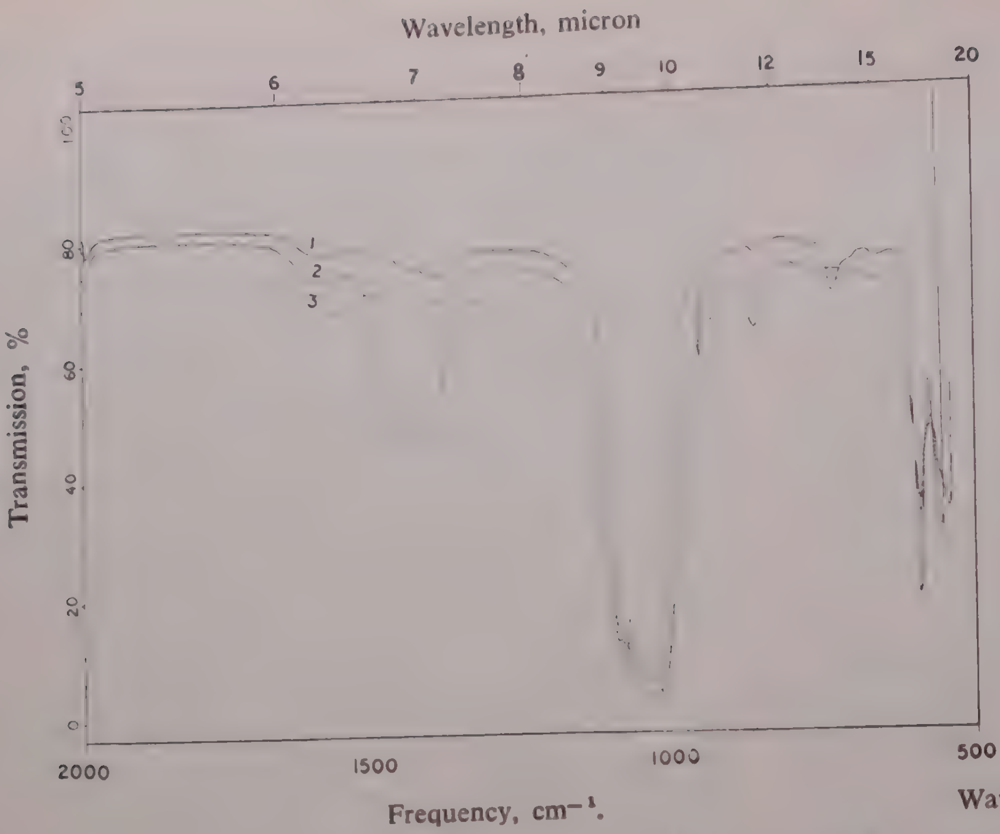

Fig. 1(a)—Infra-red Spectra
1. Synthetic Fluorapatite
2. Synthetic Carbonatoapatite
3. Synthetic Hydroxyapatite

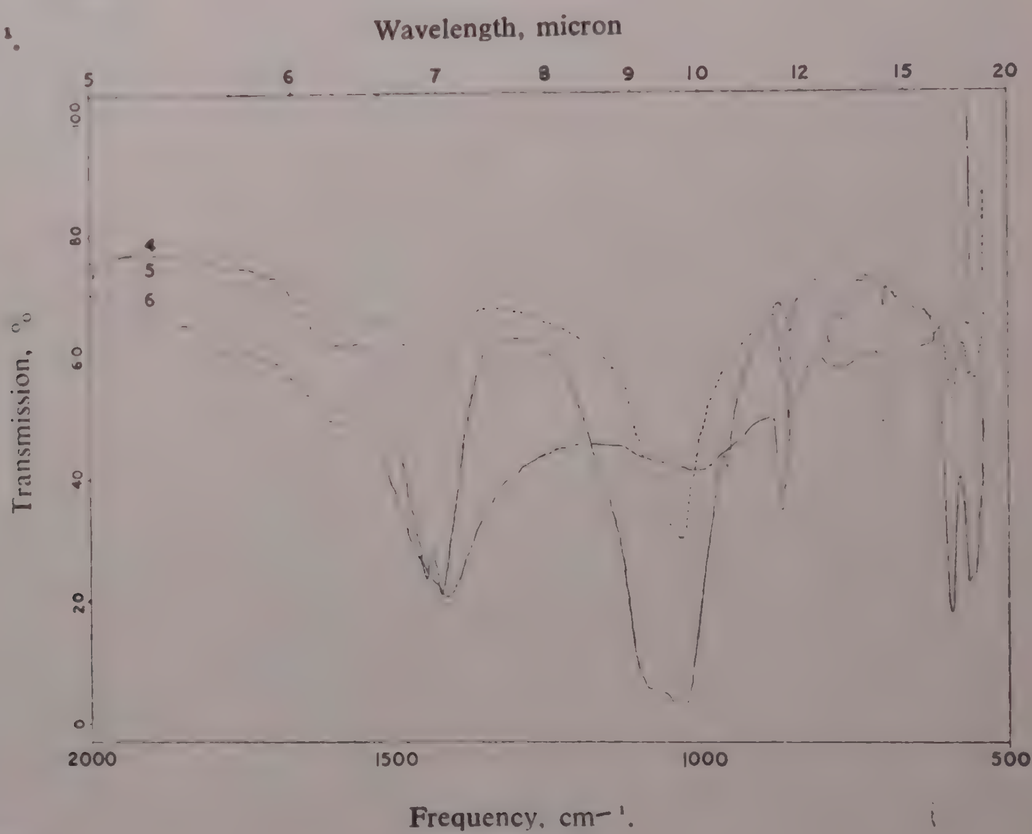

Fig. 1(b)—Infra-red Spectra
4. Jordan Rock Phosphate
5. Morocco Rock Phosphate
6. Jharbeda (India) Limestone

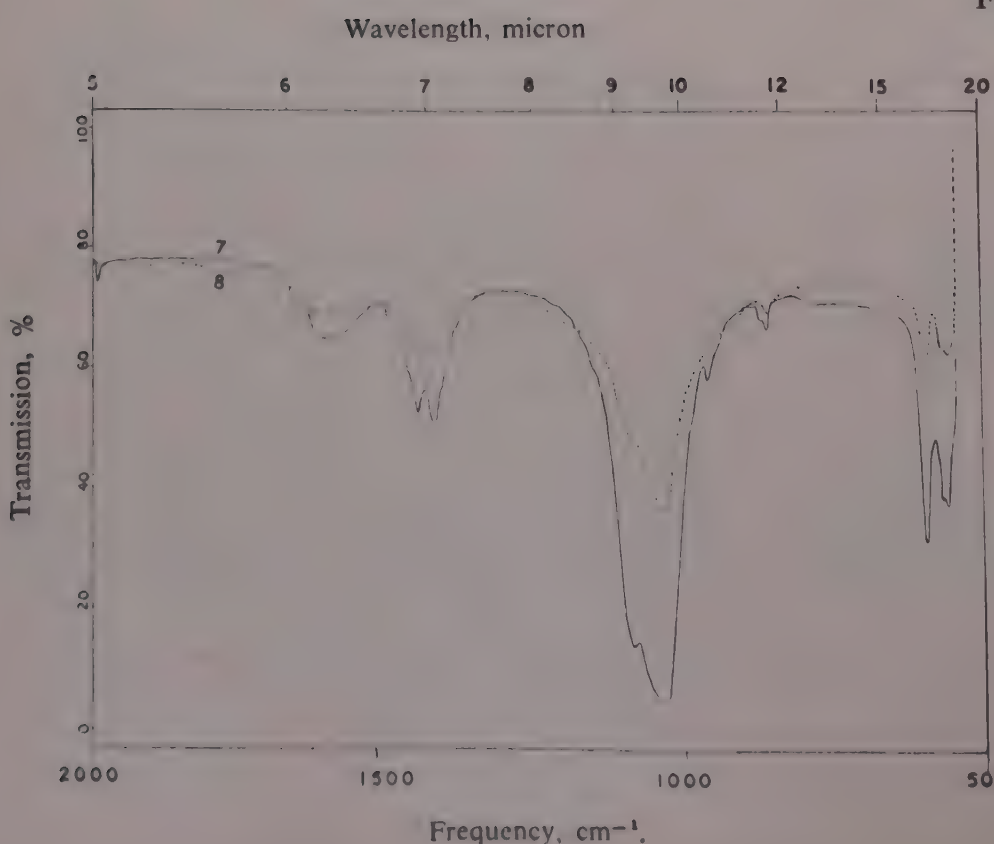

Fig. 1(c)—Infra-red Spectra
7. Makatea Rock Phosphate
8. Tunisia Rock Phosphate

TABLE 1—ASSIGNMENT OF IR BANDS FOR THE $(PO_4)^{3-}$ ION OF THE SAMPLE

Samples	Symmetry of $(PO_4)^{3-}$ ion	ν_1	ν_2	ν_3	ν_4	Ref.
Free $(PO_4)^{3-}$ ion	T_d	×	×	1080	600	8
Hydroxyapatite (synthetic)	C_s or C_2v	959	×	1090 1025	628, 602, 563	
Fluorapatite (synthetic)	C_s or C_{2v}	964	×	1090 1036	740, 602, 575	
Carbonatoapatite (synthetic)	C_{3v}	959	×	1090 1026	602, 563	
Jordan Rock-Phosphate	C_s or C_{2v}	964	×	1090 1038	800-775, 602, 575-563	
Morocco Rock-Phosphate	C_{3v}	964	×	1090 1038	602, 575-563	
Tunisia Rock-Phosphate	C_{3v}	964	×	1092 1040	602, 575-563	
Makatea Rock-Phosphate	C_{3v}	964	×	1091 1040	602, 575-563	

TABLE 2—ASSIGNMFNT OF IR BANDS FOR THE $(CO_3)^{2-}$ ION OF THE SAMPLES

Samples	Symmetry of $(CO_3)^{2-}$ Ion	ν_1	ν_2	ν_3	ν_4	Ref.
Free $(CO_3)^{2-}$ Ion	D_{3h}	—	879	1415	680	8
Calcite	D_3	—	874	1430	710	8
Aragonite	C_s	1080	866	1492	506, 711	8
Simple ionic carbonates	D_3 or C_s	1090- 1020	890- 820	1504 1470-1420	750-680	17
Jharbeda limestone	D_3	—	873	1420	710	
Carbonatoapatite (synthetic)	D_3	—	872	1462 1411	—	
Jordan Rock-phosphate	D_3	—	865	1455 1430	710	
Morocco Rock-phosphate	D_3	—	865	1453 1427	—	
Makatea Rock-phosphate	D_3	—	865	1455 1427	—	
Tunisia Rock-phosphate	D_3	—	865	1454 1427	—	

TABLE 3—CORRELATION BETWEEN C_s, C_{2v}, C_{3v}, D_{2d} AND T_d

Point group	No. of Infra-red Active Vibrations			
	ν_1	ν_2	ν_3	ν_4
T_d	0	0	1	1
D_{2d}	0	0	2	2
C_{3v}	1	1	2	2
C_{2v}	1	1	3	3
C_s	1	2	3	3

TABLE 4—CORRELATION BETWEEN D_{3h}, D_3 AND C_s

Point group	Number of Infra-red Active Vibrations			
	ν_1	ν_2	ν_3	ν_4
D_{3h}	0	1	1	1
D_3	0	1	1	1
C_s	1	2	3	3

$(CO_3)^{2-}$ ion in the apatite is that it substitutes isomorphically for phosphate ions in the lattice forming carbonatoapatite.

The occurrence of carbonate groups, on the phosphate sites will cause (a) an expansion in the magnitude of P-O distance (P-O in PO_4 is 1.54 Å and that of C-O in CO_3 is 1.30 Å), (b) change of the co-ordination of calcium about oxygen (calcium ion has ligancy of 6 in calcite), and (c) alteration of the electrostatic valency of Ca-O bond as a result of the co-ordination change.

The effect of (a) will be to produce a displacement in the PO_4 vibrations, and thereby causing PO_4 bands to shift to lower frequencies since the frequencies of the PO_4 oscillations are dependent on the equilibrium internuclear distance between P and O atoms in apatite, and those of (b) and (c) will be, definitely, to lower the symmetry of the $(CO_3)^{2-}$ ion as a result of which the forbidden vibrations of the free ion are permitted, and the degenerate modes of vibration are split.

It can be seen from the present investigation on apatite that the displacement towards the lower frequency region of the $(PO_4)^{3-}$ ion is absent and that there is no change in the symmetry of $(CO_3)^{2-}$ ion. The conclusion may therefore be drawn that the fluorine atom or the hydroxyl group in hydroxyapatite or fluorapatite, and not the phosphate group, is replaced respectively by the carbonate group to form carbonatoapatite.

In our studies on the carbonatoapatite, the splitting of the ν_3 band of $(CO_3)^{2-}$ ion has been noticed although the D_3 symmetry does not permit the same. Nakamoto[15], et al, in their studies on the carbonatoamine complexes, have observed the splitting of ν_3 band of $(CO_3)^{2-}$ ion when it is in the outer sphere of the complex, while $(CO_3)^{2-}$ having the same symmetry as that of calcite (D_3) and when this ion is co-ordinated to the metal atom (inside the co-ordination sphere), the symmetry is changed and the splitting of the degenerate mode is larger. Quagliano[16] later concluded that the splitting of the C-O assymmetric stretching (ν_3 band) indicates the metal-ligand bond. On the basis of the above explanation it can be assumed that the environment of oxygen of $(CO_3)^{2-}$ ion in carbonatoapatite is different from that of the oxygen in $(CO_3)^{2-}$ ion present both in calcite and purely ionic carbonates. Therefore, the only plausible explanation for the splitting of ν_3 band may be that in carbonatoapatite, $(CO_3)^{2-}$ ion is a part of the apatite lattice rather than present merely as an admixture of apatite and calcium carbonate and that oxygen of the $(CO_3)^{2-}$ ion is making a stronger ionic bond with calcium atom in the apatite lattice. This fact is further corroborated by the absence of a strong absorption band in the region 750-680 cm^{-1} characteristic of free carbonate ion, calcite and other simple ionic carbonates. The presence of band at 710 cm^{-1} in case of Jordan variety of rock phosphate may be due to the presence of excess calcium carbonate in the free state than what theoretically required to form carbonatoapatite.

Acknowledgements

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Interaction of Urea with Jute

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Jute bags containing urea become moist and deteriorate rapidly in humid atmosphere. This has been shown to be due to the rapid wetting of jute by urea solution and possible interaction of urea with jute. Ammonium sulphate appears to prevent rapid wetting of jute by urea solution. It is suggested that proteins present in jute play an important role in determining its wetting characteristics. Therefore, urea needs greater protection than is indicated by its hygroscopic behaviour and polythene liner appears necessary even under favourable climatic conditions.

Out of the target of 2.0 million tonnes of nitrogen for the Fourth Plan period, the indications are that urea alone may account for over 50 per cent of the proposed production of nitrogen in this country. The urea producing plants will be spread over the entire country and consumption of urea would then be restricted to the adjoining areas of the plant producing the fertilizer. It may then prove economical to draw the specification of moisture-proof bags for urea to suit local conditions rather than for worst climatic and handling conditions. Even seasonal variations may then be taken into account, as in many of the States the period October to March are less humid and even inferior bags may prove adequate for urea.

Ammonium sulphate is reasonably well protected in unlined jute bag. Hygroscopicity of urea is more than that of ammonium sulphate but is much less than that of calcium ammonium nitrate or nitro-phosphate[1]. It appeared worth-while to examine the possibility of packaging urea in unlined or paper-lined jute bags.

While testing packaging materials for ammonium sulphate-nitrate and urea, when these fertilizers were bagged in ordinary jute and crepe paper—bitumen-jute bags, ammonium sulphate-nitrate absorbed much more moisture than urea. Bag deterioration, however, occurred rapidly in the case of urea. Unlined jute bag containing urea became completely moist within a few days of the start of the test. Crepe paper—bitumen-jute bag also became moist but took a longer time. During this period bags containing ammonium sulphate-nitrate appeared dry. At the conclusion of three months' storage test, drop tests were performed and all the bags containing urea burst whereas ammonium sulphate nitrate bags remained intact.

Higher moisture uptake by ammonium sulphate-nitrate is understandable as its critical relative humidity is much lower than that of urea. But the decrease in the strength of urea bags was unexpected. It was suspected that probably a saturated solution of urea, formed on the surface of the fertilizers, was getting preferentially adsorbed by jute, and possible interaction of moist urea with jute decreased the strength of the bag.

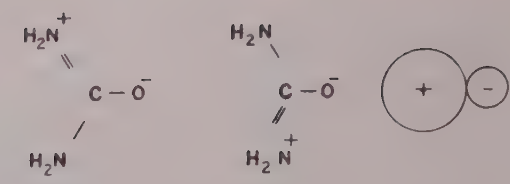
To substantiate this, it was considered necessary to study wetting characteristics of jute fibre towards solutions of various fertilizers. Seyferth-Morgan test[2], widely used to test the efficacy of wetting agents, proved convenient for such a study. This test is based on the principle that the period, that elapses between the time the fiber test piece is brought in contact with the solution and till it sinks, measures the time taken by the solution to displace the volume of air which is just sufficient to overcome the buoyancy of the test piece. Sinking time in turn is dependent on the wettability of the fibre with respect to the solution. As shown below, the densities of saturated solution vary and this must influence the sinking time, but as is seen from the results the density factor does not in any way affect our conclusions.

Saturated Solution	Sinking Time of Jute Disc.	Sp. gr. at 30°C
Ammonium nitrate	200 min.	1.33
Ammonium Sulphate	does not sink	1.25
Ammonium Sulphate-Nitrate	does not sink	1.22
Urea	1 min. 15 secs	1.16
Urea+Ammonium Sulphate (1 : 1)	does not sink	—
Ammonium Chloride	210 min.	1.08

the time taken in water—16 min.

The 'sinking time' values of circular test piece of jute cut out from the bag as given in the above table are an average of six determinations. The results indicate that jute test piece took the minimum time to sink in the solution of urea—even lower than in water. The time taken was much more in the case of ammonium nitrate and ammonium chloride. The jute test piece remained floating for 12 hours in the saturated solution of ammonium sulphate, ammonium sulphate-nitrate and urea+ammonium sulphate. It appeared that ammonium sulphate prevented jute from getting wet.

Wettability of any fabric by a solution often depends on the presence of extraneous substances present in the fibre. Pectic substances present in cotton have been found to exert profound influence on its wettability[3]. Besides cellulose and lignin jute contains 0.2 per cent nitrogen as protein[4]. Urea solution is known to be adsorbed by proteins and is effective in its denaturation[5,6]. The case of dispersibility and disaggregation of proteins by urea solution from wheat flours has been made use of in determining its bread-making potentialities[7]. Still more interesting is the fact that sulphate inhibits denaturation of proteins by urea[8]. An explanation has been put forward to explain the interaction of urea with proteins and the inhibiting effect of sulphate, according to which zwitterionic structures of urea A and B giving rise to a dipole C with a large positive charge shown below are held responsible. The sulphate ion, being large, blocks the positive end of dipole and inhibits denaturation[9]. Such resonance structures are consistent with the theory and have been experimentally confirmed.



A B C

A similarity of behaviour of jute and proteins towards urea solution and the inhibiting effect of sulphate appear to indicate that the proteins present in the jute play a major role in determining its wetting characteristics.

The wetting of the jute results in the intimate contact between the jute fibre and the urea solution, which causes deterioration of the jute bag. Thus polythene liner not only ensures protection against humidity but prevents the jute bag from deterioration and loss of the fertilizer that may be caused by even a small amount of moisture present in urea. Therefore, urea needs greater protection than is indicated by its hygroscopic behaviour and polythene liner appears necessary even under favourable climatic conditions.

The authors thank Dr. K. R. Chakravorty, General Manager for his interest in this work.

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Low Temperature Magnetic Studies on Some Fused Iron Catalysts for Ammonia Synthesis

By

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The second order transition of magnetite at about −160°C is observed to be modified due to lattice substitution and non-stoichiometry.

The present communication is a follow-up of a previous work[1] on the high-temperature magnetic studies on ammonia synthesis catalysts.

It is well-known[2–4] that magnetite undergoes a disorder-order transition in the neighbourhood of −160°C. Demenicali[5] has observed that the moment of polycrystalline megnetite remains practically constant upto about −150°C, then after a gentle rise a sharp drop is obtained at −160°C, after which the moment again shows a constancy. Our measurements on a natural magnetite also confirm this.

Since the transition is due to ordering of the Fe^{3+} and Fe^{2+} ions in the octahedral sub-lattice[4], it is to be expected that replacement of iron by diamagnetic ions will affect the nature of the transition. The catalysts studies here feature lattice substitution[1] by Al^{3+}, Ca^{2+} and Mg^{2+} ions.

The experiments were performed on a Curie balance in which the sample is suspended inside a gas-flow type cryostat designed after Bose[6]. The samples were studied within the temperature range +20°C to −180°C, using liquid nitrogen as coolant. A very weak magnetic field was used to observe the transition better.

It may be seen (Fig. 1), that in sample 1, where the Fe_2O_3: FeO ratio is nearest the stoichiometric proportions and substitution is by Al^{3+} and Ca^{2+} at octahedral sites, the thermomagnetic curve exhibits almost all the features of a natural magnetite. The exception is the hump at −172°C following the transition.

In sample 3, where the substitution is similar but non-stoichiometry is more pronounced, the nature of the transition has altered completely. It is now a gentle fall, followed by a sharp rise in the moment.

In sample 2, where the Fe_2O_3: FeO ratio is also far from the stoichiometric one, but better than in the previous case and where, besides Al^{3+}, Mg^{2+} substitution has occurred in both octahedral and tetrahedral sites, the nature of transition is still different; its sharpness being totally lost. A minimum occurred at −168°C, followed by a more or less gentle rise.

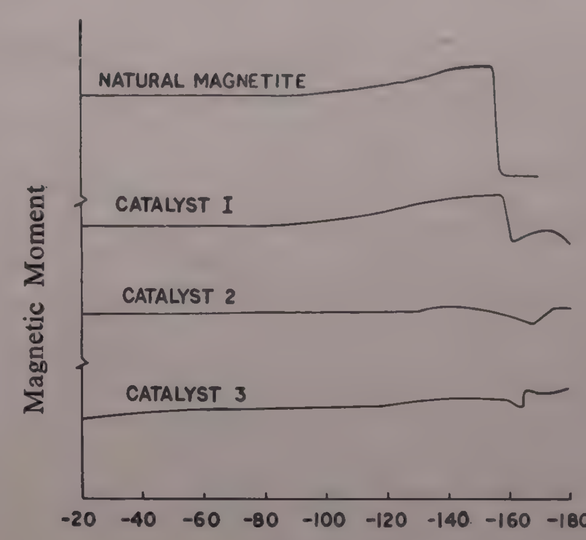

Fig. 1

The work shows that departure from stoichiometric composition and lattice substitution considerably affects the properties of magnetite.

The authors are indebted to Dr. B. K. Banerjee, Deputy Superintendent, for his guidance and interest in the work.

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ESR Observation on a Humic Acid and its Additive Compound with Urea

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A stable free radical at g =2.004 is observed in humic acids. The radical is quenched on interaction with urea, suggesting its role in compound formation.

Urea[1] is known to form additive compounds with humic acids. In a recent work Pal and Banerjee[2] postulate that urea forms an additive compound with humic acid by linking with the COOH and OH groups present. Working on humic acid isolated from the black cotton soil from Amraoti, Maharastra, they found that the pH increased and the base-exchange capacity correspondingly decreased with increasing concentration of urea and the time of interaction, thus obtaining experimental support for their assumption.

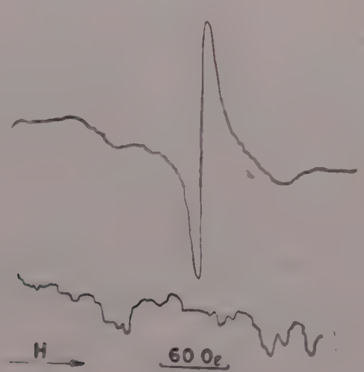

Fig. 1

The same humic acid, when studied at room temperature with a Bruker Model B-ER 402 X-band ESR Spectrometer, showed the presence of a stable free radical at g=2.004 in the upper recording (Fig. 1). In the urea-humic acid compound, however, all trace of the free radical has vanished, as can be seen from the lower recording.

The increased noise figure observed in the latter is due to the much higher amplification used. It is evident from the present observation that the free radical plays a significant role in the urea-humic acid interaction. It may be noted that the presence of the free radical was detected in humic acids obtained from other soils also.

The authors are thankful to Dr. B. K. Banerjee, Deputy Superintendent, for his keen interest in the work.

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Corrosion of Mild Steel Equipment in Degasification Section in an Ammonia Plant

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Substances, commonly used as inhibitors in aqueous solutions were not found effective when used singly in reducing corrosion of mild steel equipment in water in the degasification system in an ammonia plant. Combinations of certain substances were, however, found useful. The best inhibition was obtained with a mixture of sodium nitrite (0.8 g./100 ml.) and a soluble oil (0.2 ml./100 ml.)

Corrosion has occurred in mild steel equipment in contact with water in the degasification system in the ammonia plant at Sindri. In this plant, carbon dioxide is removed from the synthesis gas by scrubbing with water at a pressure of about 285 lb./sq. in. and water laden with carbon dioxide is degasified in two stages—first, at a pressure of 30 lb./sq. in. and then at 2 to 3 in. of water. The evolved gas, containing mainly carbon dioxide along with small quantities of hydrogen, methane, carbon monoxide and sulphuretted hydrogen is used for the preparation of ammonium carbonate solution for reaction with gypsum. Corrosion of mild steel in presence of dissolved carbon dioxide and sulphuretted hydrogen has been reported by a number of investigators[1–3]. The present study was undertaken to find out suitable inhibitors for preventing corrosion of the mild steel equipment in the above system.

The weight-loss experiments were carried out at 40°C by the same method[4] with mild steel test coupons immersed in water collected from the degasification system. The impure carbon dioxide gas obtained after degasification was continuously passed through the water. Experiments were carried out both in presence and absence of various inhibitors.

A typical analysis of the impure gas from the degasification unit is as follows: CO_2—88.0; O_2 0.4; CO-0.8; H_2-5.6; CH_4-0.6; N_2-4.6; and H_2S-0.01 per cent.

Water from the degasification unit was of the following range: pH 6.9 to 7.3; P nil; M 102 to 165 mg/l. Cl 20-30; Ca 20-30; SO_4 98-130; H_2S 10-14; CO_2 4-6; and TDS 360-430 mg/l.

The results (Table 1) show that no substance when used alone is much effective as an inhibitor. Chromates are

TABLE 1—Corrosion and Inhibition of Mild Steel in Degasification System Water in Presence and Absence of Inhibitors

(Duration of test—24 hr.)

Nos.	*Inhibitors Used*	*Corrosion rate mg/sq.dm/day*
1.	No inhibitor	90.5
2.	Sodium Benzoate (0.4 gm/100 ml)	109.8
3.	Sodium Nitrite (0.4 gm/100 ml)	320.7
4.	Ammonium Thiocyanate (0.2 gm/100 ml)	131.3
5.	*Soluble Oil (0.2 ml/100 ml)	65.0
6.	Ammonium Thiocyanate (0.2 gm/100 ml)+ Soluble oil (0.2 ml/100 ml)	38.0
7.	Urotropine (0.5 gm/100 ml)+Sodium Benzoate (0.5 gm/100 ml)	100.0
8.	Urotropine (0.5 gm/100 ml)+Sodium hexametaphosphate (50 mg/litre)	59.0
9.	Sodium Benzoate (0.4 gm/100 ml)+Soluble oil (0.2 ml/100 ml)	57.4
10.	Sodium Nitrite (0.4 gm/100 ml)+Soluble oil (0.2 ml/100 ml)	18.0
11.	Sodium Nitrite (0.8 gm/100 ml)+Soluble oil (0.2 ml/100 ml)	7.3
12.	Sodium Nitrite (0.2 gm/100 ml)+Sodium Benzoate (0.4 gm/100 ml)+Soluble oil (0.2 ml/100 ml)	9.6
13.	Sodium Nitrite (0.2 gm/100 ml)+Ammonium Thiocyanate (0.2 gm/100 ml)+Soluble oil (0.2 ml/100 ml)	14.9

*'Gulf Sil' brand

not suitable as they are readily reduced to insoluble trivalent compounds by sulphuretted hydrogen present in the water. Certain common inhibitors, like sodium benzoate, sodium nitrite, etc., actually increase the rate of corrosion of mild steel in water from the degasification system. However, satisfactory results were obtained when combinations of certain substances were employed. Thus, the combinations, viz. (a) soluble oil +ammonium thiocyanate; (b) soluble oil +sodium nitrite; and (c) soluble oil +sodium nitrite +sodium benzoate, gave satisfactory inhibition. The best result was obtained with the combination 0.8 g./100 ml. of sodium nitrite +0.2 ml/100 ml of soluble oil; in this case the corrosion rate was reduced from 90.5 to 7.3 mg./sq. dm./day.

The authors wish to thank Dr. K. R. Chakravorty, General Manager, for his interest in this work.

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CORRIGENDA

Ref. Paper:	'Studies on the Relative Efficiencies of Nitrophosphate and other Nitrogenous and Phosphatic Fertilizer Combinations I' by S. P. Dhua and B. Chowdhury, TECHNOLOGY, Vol. 3(2) (1966), 78-86
Figs. 11 & 12	on p. 83 along ordinate 50 + 100 lbs. be read as 50 and 100 lbs. N + P_2O_5 be read as N and P_2O_5
Fig. 13	p. 84 $SPAS_2$ be read as $SPAS_1$ along ordinate 50 + 100 lbs. be read as 50 and 100 lbs. N + P_2O_5 be read as N and P_2O_5
Fig. 14	p. 84 along ordinate N + P_2O_5 be read as N and P_2O_5
Figs. 15 & 16	p. 84 along ordinate 50 + 100 lbs. be read as 50 and 100 lbs.
Fig. 17	p. 84 along ordinate straws be read as straw

Notes & News

SNAM Progetti's Urea Process

SNAM Progetti S.P.S. of Milan, Italy has developed one stage, high pressure carbamate recycle process for the production of urea with minimum biuret content (0.3-0.7% by weight) and urea conversion efficiency of 98% involving less steam consumption and less investment costs.

The process is based on the principle that carbamate in the presence of pure ammonia or carbon dioxide vapour phase, can be dissociated at any pressure. The carbamate contained in the reactor effluents is decomposed and separated from urea solution in a specially designed "carbamate decomposer" where a stream of pure ammonia allows the carbamate decomposition at a high pressure (100 to 150 kg/Cm²/g).

Carbamate solution, obtained in the carbamate condenser, is available at high pressure and can be recycled to the reactor by gravity, thus eliminating the carbamate pumping operation.

To maintain the reactor pressure of the carbamate solution, a one step centrifugal pump could be substituted for the traditional type pump with important saving in operating and investment costs.

Process Description: The raw materials, CO_2 and NH_3 and recycle streams NH_3, and carbamate solution are fed to the reactor which can operate 100-150 kg/Cm²/g or 200-250 kg/Cm²/g. according to the two different applications of the process CO_2 by compressor and NH_3 by a pump. A molar ratio NH_3/CO_2 of 3.5 : 5 is maintained in the reactor.

Part of the free ammonia contained in the urea solution, coming from the reactor, is separated to be used as "stripping medium" in the "carbamate decomposer". In this vessel which operates at 100-150 kg/Cm²/g. and 160-200°C urea solution is freed from all carbamate and from a large quantity of ammonia. The vapours pass to the carbamate condenser where a hot carbamate solution is formed at 100-150 kg/Cm²/g. This solution can be recycled to the reactor by gravity a by pump. All the heat developed in the carbamate condenser is recovered as steam and thus steam consumption is considerably reduced.

The urea solution formed finally passes through a series of vessels to recover the contained residual ammonia. The excess of ammonia in different steps of thee SNAM process is important because of obtaining high conversion rates: the some ammonia, already used in the reactor, afterwards passes to the "carbamate decomposer" as stripping medium to obtain the complete carbamate decomposition at high pressure. Finally the ammonia permits high temperatures in the carbamate decomposer, without any corrosion problem and biuret formation.

[Nitrogen, No. 41, June 1966, p. 34]

Mitsubishi Wet-Phosphoric Acid Process

Two Japanese professors of Tohoku University have developed a wet phosphoric acid process with 98.5% of P_2O_5 recovery and a high quality large crystals of by-product gypsum suitable for plaster board are obtained. Several phosphoric acid plants of Japan have applied this process with satisfactory results.

In the commercial process adopted by Mitsubishi Chemical Industries Co., phosphate rock is pulverized and then kneaded in a premixer with mixture of sulphuric and recycled phosphoric acids. It is claimed that the plant can even handle rock phosphate grades that contain iron, aluminium or organic impurities.

Decomposition of the rock takes place at 203°F, this high temperature being maintained by adding the sulphuric acid in concentrated 98% strength and diluting it with water directly to the premixer. At this stage Mitsubishi adds activated silica to take up organic matter that would otherwise hinder the growth of gypsum crystals. In addition, use of sulphuric acid in excess of stoichiometric amounts dissolves any iron and aluminium impurities and so prevents these from interfering with crystal growth.

Calcium sulphate in the above process is formed as the hemihydrate $CaSO_4 \cdot \frac{1}{2} H_2O$ and recrystallization to the dehydrate form (gypsum) takes place at 140-150°F by circulating the reaction slurry through ageing and cooling tanks.

A cooler evaporator in the recycle loop continuously concentrates the slurry on route to the cooling tank which permits the high rate of recrystallization to large gypsum particles, and savings in equipment cost since the vessel size is reduced.

Phosphoric Acid: Separation of phosphoric acid, as 30% P_2O_5 product, takes place under vacuum in a horizontal filter with a three step raosting device of Mitsubishi design. The gypsum cake moving from one filter cell to another is washed at first with weak recycled acid and then in the last stages with water. The gypsum obtained is pure enough for commercial use to cement and plaster manufacturers.

In the Mitsubishi design system of instrumentation, operation can be controlled with greater case and precision.

[Phosphorus and Potassium, No. 22, April-May 1966, p. 32]

42% P_2O_5 Phosphoric Acid in High Yields

A high concentration 42% P_2O_5 phosphoric acid while keeping the yields above 97% by using a two-stage chilling from temperatures of hemihydrate crystallization to temperatures from gypsum crystallization, and simultaneously recycling the solution from filtering gypsum, has been developed by using Singmaster and Breyer's (New York) new process.

A special vacuum slurry cooler with a large internal circulation is a key feature

providing cooling by liquid-liquid contact in the process. Formation of scale that forms on the inside surfaces of once-through cooling vessels is avoided by feeding the hot slurry directly into a large circulating body of drilled slurry. Solids form within the chilled liquid. In this process the hot slurry is pumped up into the bottom of a vacuum tank directly below an agitator. Heat from the hot slurry is removed from the surface of the liquid in the form of water vapour evaporated off to a barometric condenser. As the total volume of liquid is very large the temperature drop at the slurry surface is only of a degree or so.

The vacuum cooler is used twice in the S and B process; first, to cool the hot slurry from digesting raw phosphate rock to 205°F and 42% P_2O_5 phosphoric acid with no sulphuric acid present; and second to cool the slurry from redigesting the calcium hemihydrate to 165-170°F with some 20-25% P_2O_5 phosphoric acid and 5-10% sulphuric acid present in solution. It is this separation from hemihydrate crystals of calcium sulphide that accounts for the high concentration of phosphoric acid obtained. Calcium sulphate hemihydrate can be crystallized out of phosphoric acid solution at 190-350°F and at P_2O_5 concentrations that are over 50% while the gypsum crystals can be formed below 140°F at phosphoric acid concentrations corresponding to less than 40% P_2O_5.

In the S and B technique, crushed phosphate rock is fed into the hemihydrate digester and mixed with fresh sulphuric acid plus solution recycled from the gypsum filters. Digested slurry is pumped through the first vacuum cooler to the hemihydrate filter, where the 42% P_2O_5 phosphoric aicd is separated from the solids. These solids are then mixed with additional sulphuric acid plus recycle solution from the gypsum filter in the gypsum digester, fed through the gypsum slurry vacuum cooler to the gypsum filter where the gypsum by-product is separated from the solutions.

[Phosphorus & Potassium No. 22, April/May 1966, p. 35]

Non-Sulphur-Sensitive Autothermal Gas Synthesis Process Developed by BASF

Badische Anilin-Und Soda Fabrik AG. (BASF) of West Germany has developed a novel catalytic process of cracking naptha to yield synthesis gas which does not require pre-treatment, e.g. desulphurization of the naphtha and does not produce carbon black. It operates at atmospheric pressure which is distinct from the present trend towards high-pressure reforming. It yields better synthesis gas than under high pressure processing and that the process consumes less oxygen and needs less catalyst replacement.

The process, which is an adaptation of an older BASF synthesis gas route based on the methane feedstock, is essentially a combination of partial oxidation and steam reforming and requires oxidation of some of the naphtha feedstock with oxygen or oxygen-rich air: this supplies heat for the subsequent endothermic reaction of the remaining hydrocarbon with steam.

BASF utilizes a more feasible preheat temperature level of between 300 and 750°F with 0.6-1.3 lb/mol. steam per lb/atm. of carbon added to ensure safe operation. In this temperature range less steam is required.

In the new furnace design a shorter fine interval between mixing and partial oxidation at the platinum catalyst was found to completely eliminate the formation of flames and carbon black.

BASF platinum catalyst is unaffected by the sulphur content of the naphtha. Previously the reforming catalyst used consisted of a ceramic carrier with a nickel coating, but this was severely damaged by sulphur, so that in continuous operation the catalyst process became purely thermal cracking. Temperature rise at the catalyst exist was so great that irreversible damage—due to crystallization was carried. BASF has, therefore developed new homogeneous nickel catalysts that exhibit only minor poisoning effects and which are mostly reversible.

With a constant sulphur content in the naphtha feed, temperature at the catalyst-bed exit rise only during the first hours after start-up and then remains almost stable.

(Nitrogen, No. 41, June 1966, p. 37]

Design Criteria for Large Complete Recycle Urea Plants

For achieving economical commercial production of urea, new processes are being developed on the basis of carbamate solution recycle. To derive the maximum benefits of producing urea, a large 15,00 metric tons/day single train urea plant is now engineered. A single stream plant would require one of each the major items of equipment items such as the reactor, decomposers and carbamate condensers. The size of the reactor for 1500 t/d production capacity becomes fixed when the feed mol proportions and the operating temperature are established.

The operating pressure is determined by choosing a practical loading density. A high conversion of carbamate to urea per pass is achieved by providing reactor internals. The design of the reactor and its internals is based on a knowledge of the process dynamics.

When ammonium carbamate decomposes, a large volume of gas consisting of ammonia, carbon dioxide and water vapour is stripped from the reactor effluent. A two-phase fluid results, and the velocity in the tubes increases as decomposition progresses. Liberal design factors cannot be allowed if the size and cost of the decomposers are to be minimized. It is necessary to know exactly what the over-all heat transfer co-efficients are.

The heat liberated by the condensation of ammonium carbamate and its dissolution in the recycle water along with free ammonia can be extracted in many ways. Indirect cooling of the solution in heat exchangers by use of cooling water; counter current contact with reflex ammonia and direct injection of liquid ammonia are some of the means usually employed. The contacting of gas and liquid can be accomplished by the use of a combination packed and plate tower design. Since the second stage carbamate condenser operates at low pressure, there are no problems in designing this vessel for a 1500 t/d plant. The first stage carbamate condenser which operates at a higher pressure can also be kept within dimensions which are not extraordinary. The sizes and weights of the condensers will present problems in shipment and erection.

For 1500 t/d production centrifugal compression should be considered. Processes which operate without using external water for carbamate recycle will not require high capacity carbamate recycle pumps.

By designing an improved complete recycle urea plant, the investment cost and utility requirements can be greatly reduced.

About 65% of electric power consumed in a urea plant is due to CO_2 compres-

sion. In Chemico urea process steam and cooling water consumptions are lowest because of using unit heat recovery technique and the lowest percentage of water in the carbamate recycle solution.

In the new Chemico recycle urea process which is called a thermo-urea process, the entire concept is based on thermodynamics and urea recycle process has been optimized on the basis of vapour liquid equilibria principles, where heat of condensation of carbamate is recovered at a high temperature level and utilized to produce steam required for decomposition and urea finishing. Here many process steps and corresponding equipment are eliminated; cooling water requirements are eliminated and the steam requirements are satisfied as a result of recovering the heat of condensation of carbamate at a high temperature level. The heat equivalent to the extra power consumed in adiabatic compression versus polytropic compression is reclaimed partly by preheating feed ammonia and carbon dioxide and partly by the production of more steam. Large tonnage urea production by the Chemico thermo urea process satisfies this requirement.

A preliminary cost study indicates that the investment for a plant based on the Chemico thermo-urea process will be much less than for a plant employing the carbamate solution recycle technique.

[Hydrocarbon Processing and Petroleum Refiner, 45 (1966), **2**, 129]

Shell Sulfinol Process for Acid-Gas Removal

The shell sulfinol process is a new method very suitable for handling very sour natural gas because of its greater gas-heating capacity, lower solvent circulation, lower heat requirements and lower rates of solvent degradation. In these respects the shell sulfinol process is better than the wellknown aqueous MEA process. The process is also of considerable interest in many solutions which do not involve very high partial pressures of acid gases.

As a solvent sulfolane's capacity for H_2S absorption is nearly eight times that of water at all partial pressures. It is also a good physical solvent for CO_2, mercaptans and carbonyl sulphide.

When an alkylamine is added to sulfolane, the alkalinity of the amine leads to high solubility at low partial pressures, as in the case of aqueous MEA, while at high partial pressures the solubility of H_2S exceeds that in sulfolane. Thus, in the sulfinol process there is a solvent which is nearly equivalent to aqueous MEA in H_2S capacity at very low partial pressures. It is much superior at high partial pressures.

With the sulfinol solvent, the acid-gas equilibria are much more sensitive to temperature, so it is easier to regenerate. Since fewer gallons of solvent need to be circulated, the stripping steam requirement per unit of acid gas is strikingly low.

Pilot Plant Operations: Pilot plant studies were conducted in a mobile unit to study the effect of sulfinol process. The equipment was built of stainless steel and carbon steel. There was no decrease in gas-treating capacity of the absorber during a two-month period, actually, there was a 15% increase in capacity.

It permitted nearly twice much gas flow at the flood point. By chemical analysis sulfinol compound was found to be exceedingly stable both chemically and thermally. In commercial service as an aromatic extraction solvent under much more severe conditions sulfolane shows virtually no deterioration and none is expected in gas treating service.

Corrosion of carbon steel specimens was low with sulfinol, except in the hot fat solvent region where rates were still one fourth those observed with aqueous MEA.

Another series of pilot-tests conducted near Edmonten Alta, show that it is a better absorber than MEA.

The sulfinol process usually absorbs more than 90% of all mercaptans while treating for H_2S and CO_2 with no increase in solvent flow or heat duties. The process thus offers an attractive solution to the mercaptan problem. Removal of 96% methyl mercaptan can be obtained when processing a synthetic gas mix to which a controlled amount of methyl mercaptan had been added.

The first commercial application of sulfinol process for treating acidic gases went into operation at the person gas plant. The process efficiently removes hydrogen sulphide, carbon dioxide, carbonyl sulphide and mercaptans from acid gas.

[Sulphur, No. 62, Feb./March, 1966, p. 29]

Removal of Hydrogen Sulphide and Mercaptans by the Lacy-Keller Process

Lacy Research and Development Inc. U.S.A. has developed a process of removal of hydrogen sulphide and mercaptans from contaminated sour gas without the removal of carbon dioxide and without lessening the volume of the gas stream at 10% of the operating cost of amine plants.

A chemical solution, details of which have not been revealed, is used to react with the sulphur compounds. It is run to two contactor columns where it reacts with H_2S and mercaptans to produce colloidal sulphur which is dispersed in the solution. This solution then passes out of the bottom of the contactor columns to a bank of flotation cells, where sulphur is flocculated, rises to the surface and is carried off as a thick slurry to the filter. The filtrate, i.e. the solution is pumped through a regeneration cycle to the contactors in a closed system.

Two plants in U.S.A. are following this new process. At the Long Beach plant up to 300 lb/day of sulphur from 12 to 20 mm. c.f.d. of incoming gas can be removed. The capacity of a plant using the new process is related to the amount of sulphur to be removed, rather than to the volume of gas to be processed. Thus the lower the sulphur content, the higher the volume of gas that can be processed without increasing the number of regeneration cells. Stainless steel is used for most of the gas handling equipment. The contactors are lined with baked-on epoxy. In the Long Beach plant CO_2 which is not removed is used as saleable gas and provides a good return.

Limitations to the process are that it will not remove unoxidizable compounds and that it is not considered economical unless it removes more than 1 ton of sulphur daily.

[Sulphur, No. 62, Feb/March, 1966, p. 35]

Agricultural Developments During Fourth Plan

Agriculture claims top priority in the Fourth Plan Outline. The main approach is five-fold: (1) To make an intensive use of the new strategy of intensive cultivation in areas where irrigation is assured. Improved seeds of foodgrains will be used in 274 million acres of land of which 32.5 million acres will be under the new high yielding varieties by the end of the

Fourth Plan; (2) to make available to the farmer the essential inputs to increase agricultural production—fertilizer, better seeds, pesticides, technical advice and know-how and so on; (3) to set up a network of agroeconomic industries which will produce tractors, better implements, fertilizer, pesticides, etc.; (4) to concentrate on soil and moisture conservation measures and on drought-resisting crops, pasture development and animal husbandry in areas where irrigation is difficult and rainfall precarious; and (5) to make agriculture export-oriented as far as possible by boosting up the production of exportable commercial crops and to enable agriculture to supply basic raw materials to domestic industries.

The Fourth Plan also emphasizes th- importance of giving much greater assiste ance to the small peasant and includes programmes to help the small farmer and to persuade them to organize their activities on cooperative lines.

In the five decades before the beginning of planning, Indian agriculture crawled at the average rate of less than one per cent per year. In the 15 years of planned development the rate of growth rose to 2.8% in the First Plan, 3.9% in the Third Plan. The Third Plan progress was unsatisfactory due to reasons already mentioned but there was no stagnation.

In the field of agriculture the major Fouth Plan targets are as follows:

	IV Plan	III Plan
Foodgrains output	120.0 m.tonnes	90.0 m.tonnes
Minor irrigation	17.0 m.acres	13.10 m.acres
Major and medium irrigation (Addl.-Gross)	9.0 m.acres	(Potential) 5.4 m.acres
Soil Conservation	20.0 m.acres	9.8 m.acres
Land reclamation	2.5 m.acres	4.20 m.acres
Fertilizers	3.35 m.tonnes	0.84 m.tonnes

The following are the major heads of outlay sectorwise:

Agricultural production	Rs. 720 crores
Minor irrigation	Rs. 520 ,,
Soil Conservation	Rs. 218 ,,
Animal husbandry	Rs. 142 ,,
Dairy and milk development	Rs. 59 ,,
Fisheries	Rs. 113 ,,
Forestry	Rs. 122 ,,

Also during the Fourth Plan: 137 million acres are to be brought under plant protection schemes. Fruits are to be raised in 40 lakh acres. 10,000 gardeners will be trained for kitchen-gardening. Admission to agricultural colleges will be 9,500 in 1966-67 and 11,500 in 1970-71. Special facilities will be provided for the education of farmers. Agricultural research will be considerably expanded with special emphasis on the development of drought-resisting varieties for lands without irrigation or with poor rainfall, and on scientific studies on soil and water management. Intensive fodder development will be introduced in 30 intensive development projects and 300 key-village blocks. 900 markets will be developed into regulated ones in addition to the 1,600 markets already regulated. 600 grading units will be set up. Agricultural processing industries will be set up in villages.

By the end of the Fourth Plan it is hoped that the country will produce 35,000 agricultural tractors, a great many of them in the public sector units to be set up. It is proposed to build up buffer stocks of 6 million tonnes of foodgrains by the end of the Fouth Plan.

There will now be a national milk policy to complete and consolidate the milk supply schemes already set up, to expand the milk plants, and the milk supply schemes wherever possible and set up rural dairy centres, expand the manufacture of dairy equipment and stores, develop cattle, and encourage rapid growth of co-operative diaries.

Fish production will go up to 15.3 lakh tonnes by 1970-71 from 11.50 lakh tonnes at present.

[Yojana, Sept., 4, 1966, p. 18]

Ammonia Synthesis Catalysts

The recent researches on the ammonia synthesis catalysts and the functions of promoters have been reported by Dr. R. Krabetz and C. I. Peters of the Badische Anilin and Soda Fabrik A.G. As the requirements placed upon the ammonia catalyst became increasingly stringent its composition became more and more complex. The first BASF technical catalyst consisted essentially of iron and two promoters (alumina and potassium oxide), calcium oxide was later added to give a promoted catalyst. Recently, quadruply and quintuply-promoted catalysts containing magnesium or beryllium and silica as well as alumina, potassium oxide and calcium oxide have gained technical importance.

Catalytic activity reaches a maximum at 3% alumina, but beyond this concentration the increase becomes slower. The principal functions of the alumina is to stabilize a porous iron structure with a large surface area. The 3 to 4% alumina is probably the quantity which is dissolved in the magnetite lattice and which separates out at the surface on reduction as an intimate mixture with the iron atoms. A further portion of Al_2O_3 makes no substantial contribution to the formation of the surface area.

Another function of the alumina is probably to prevent the thermal transformation of the particularly active crystal faces. When magnetite is carefully reduced at 300°C, the reduced iron chemisorbs roughly one molecule of carbon monoxide per atom of iron, when it is assumed that the exposed crystal face is the face. If the catalyst is then heated to 600°C, the quantity of carbon monoxide chemisorbed per atom of iron decreases by 50%, which indicates that the iron surface has been sintered to more closely packed crystal faces. The quantity of carbon monoxide chemisorbed on the sample containing 3% alumina was the same as before and after heating at 600°C.

The sensivity of the catalyst towards inactivation by sulphur or chlorine decreases with increasing alumina content. Small quantities of potassium added increase the activity of the catalysts which contain difficult reducible oxides of groups III and IV. The catalytic activity of pure iron is reduced on introduction of potassium oxide. Any increase in the potassium content simply leads to an increase in its concentration at the surface.

In contrast to the situation with singly promoted catalysts, here the action of the promoter is not related to the total surface area or to the free iron surface area both of which decrease with increasing potassium content.

The observation that samples containing potassium have smaller internal surface areas than those without it indicates that potassium promotes recrystallization of the iron crystallites and this is particularly noticeable when the reducing or synthesis gas contains oxygen compounds.

The pore size distribution in $Fe—Al_2O_3—K_2O$ catalysts is influenced by their potassium content. The optimum potassium content for maximum ammonia

yield varies from one type of catalyst to another. There is a close relationship between the structure and properties of the reduced catalyst and the distribution of the potassium in the unreduced sample.

Potassium also changes the resistance of the catalysts toward poisons, like sulphur, than samples activated with alumina alone. Conversely, potassium increases the sensivity of the catalysts toward gaseous oxygen compounds.

Catalyst activated with calcium or magnesium alone have smaller surface areas and poorer catalytic activity than samples activated with alumina. However, alkaline earth oxides in combination with K_2O and Al_2O_3 have gained technical importance. Catalyst with alumina and K_2O with increasing calcium oxide were reduced at 500°C and then aged at 600°C in synthesis gas containing oxygen, and it was found that the sample with the highest calcium content was least damaged by heat treatment.

Catalysts containing calcium are also less sensitive towards irreversible poisoning by H_2S or chlorine compounds. Magnesium did not have the same effect as calcium catalysts containing alumina and potassium. If part of the calcium in a catalyst activated with 2.5% alumina, 0.5% potassium oxide, and 2.0% calcium oxide, is replaced by magnesium, the activity is increased. The ammonia yield reaches a maximum when about half of the calcium has been replaced by magnesium.

The silica evidently leads to a more uniform distribution of the potassium inside the secondary particles, probably by formation of potassium alkaline earth silicates. The total surface area increases with the silica content, but the percentage of the total surface covered with free potassium and alkaline earth metals decreases. The catalytic activity passes through a maximum.

Thus, a better distribution of potassium, alumina, and silica during the reduction stabilizes reduced iron structures with larger surface areas, the catalytic activity depends, however, not only on the total surface area, but probably also on the concentration of free potassium in the surface, which is greatly reduced by silica.

As with the simpler $Fe\text{-}Al_2O_3\text{-}K_2O$ catalysts, the catalytic activity passes through a maximum at a certain potassium content, which increases with the silica content. Thus, while only 0·4% potassium oxide is required for maximum conversion with a catalyst containing no silica, 2% potassium oxide is necessary in the presence of 4.2% silica.

Best catalysts always have potassium concentration of 25 to 30% on the surface, irrespective of the absolute quantities of silica and potassium oxide present.

[Nitrogen, No. 41, 1966, p. 38]

News in Brief

Effect of Fertilizers on Paddy in Saline Solution

The effect of ammonium sulphate and superphosphate on paddy yield in saline coastal soil of West Bengal has been studied at the Saline Rice Station, Canning, using 3 levels of nitrogen and phosphoric acid. Ammonium sulphate and superphosphate have given increased yield when applied singly and also in conjunction with each other. Nitrogen at 40 kg/ha. and phosphoric acid at 20 kg/ha. has been found to be the most economical fertilizer combination.

Studies at the same Station have also indicated that at 1 per cent salt solution, some varieties of rice gave cent per cent germination and others below 50 per cent with delay in germination. 2 per cent salt solutions showed very poor percentage of germination.

[Salt Research & Industry, 3 (1966), 1, 9]

CO-Conversion Catalysts

In the conversion of natural gas in U.S.S.R., the previously used one stage method for shift reaction has been replaced by a two-stage one because of economics of steam consumption and higher degree of conversion (up to 95 per cent) on Fe-Cr catalyst SINI 482. The space velocities used are 300-400 $hr.^{-1}$ at atmospheric pressure and 1300-1600 $hr.^{-1}$ at elevated pressures (16-18 ata). Recently some new and highly effective catalysts based on iron oxides have been developed by the Soviet research institutes such as IICT**-45 and IICT**-565. On these, equilibrium is attained at 400-420°C. A Zn-Cr-Cu catalyst which converts carbon monoxide at such low temperatures as 200-250°C has been developed by the State Institute for Nitrogen Industry (SINI).

[Chem. Age of India, 17 (1966), 3, 182]

** Ivanovo Institute of Chemical Technology.

World Nitrogen Industry

During 1963-64, world production of nitrogen amounted to 18,036,000 tons, or an increase over 1962-63 of 12.9 per cent. Consumption at 17,926,000 tons showed an increase of 12.1 per cent. The rate of growth in the major trading areas was: N. America, including Canada, production 13.5 per cent, consumption 15.6 per cent; W. Europe production 10.4 per cent, consumption 6.8 per cent; E. Europe production 18 per cent, consumption 19.7 per cent; and Asia including Japan, production 8.6 per cent consumption 7.9 per cent. Excess of world production over consumption during 1963-64 amounted only to 0.6 per cent, and created a shortage of supply.

The greatest shortage arose over calcium ammonium nitrate due to increase in demand for it as well as due to some firms switching over to the production of urea. Urea was the next shortest product followed by ammonium sulphate. It is estimated that world production and consumption of nitrogen will continue to increase at an accelerated rate during 1964-65 by approximately 11.9 and 11.5 per cent to 20,189,000 and 19,992,000 tons respectively.

[Fertil. & Food. Stuff J., 62 (1965), 5, 194; Abstr. FAI Abstr. Serv., 4 (1965), 10-12, 11]

Potassium Chloride from Mixed Salt Using Soda Ash Plant Wastes

The mixed salts of sea bitterns treated with distillery waste liquor from soda ash plant (having 8 per cent $CaCl_2$) equivalent to the total sulphate content of the mixed salt. Gypsum is precipitated in a very fine form and removed by filtration. The desulphated filtrate on solar evaporation to 32°Be, the remaining potassium chloride separates as carnallite. Overall recovery of potassium chloride as NaCl+KCl mixture (65 per cent) and carnallite (20 per cent) is 85 per cent. The potassium chloride recovery is further improved to 90 per cent if the washings from gypsum are added to the filtrate. Based on experimental calculations, 5,000 tonnes of mixed salt and 1,08,560 kilolitres of distillery waste liquor processed in 125, pans of 40×40 ft. will yield in one season 1,000 tonnes of potassium chloride as NaCl+KCl and carnallite.

[Salt Research & Indus., 3 (1966), 80-81]

Potash Manufacture

A plant to manufacture potassium chloride, set up by the Central Salt and Marine Chemicals Research Institute, Bhavanagar in collaboration with M/s United Salt and Industrial Works, has gone into stream at Kandla. The plant is based on a process developed entirely in the Institute and equipment and machinery used are completely indigenous. The process utilizes mixed salt obtained by solar evaporation of bittern.

[TICCI News letter, 1 (1966), 3, 1966]

Manganese Sulphate from Indigenous Ores

Manganese sulphate is used extensively for stimulating plant growth and combating chlorosis of various crops. It greatly increases the yield of tomatoes and crops like spinach corn, soya bean, etc. It is also used for direct spraying for counteracting deficiencies of manganese in soil. Fertilizer grades of magnanese sulphate are usually available in 65-75 per cent grades containing some amounts of ammonium sulphate.

A batch process has been developed at CERI, Karaikudi, for the production of manganese sulphate monohydrate of 93-96 per cent purity from manganese ores. The ore is mixed with a reducing agent (charcoal or coal) and roasted at a moderately high temperature followed by leaching with dilute sulphuric acid. The leached liquor after removal of impurities is concentrated to saturation when crystals of manganese separate out. The recovery is about 60 per cent.

[TICCI News letter, 1 (1966), 2, 2]

Potassium Sulphate

The Central Salt and Marine Chemicals Research Institute at Bhavanagar have surveyed the brines from 23 inland salt works in the Little Rann of Kutch for proposal for exploitation of their bitterns for setting up a factory at Kharaghoda for the production of potassium sulphate, which is preferred to potassium chloride as certain crops, viz. tobacco, potato, sugarcane, citrus fruits etc., cannot tolerate chloride ions. The present potential for potassium sulphate manufacture from salt works in the Little Rann is 6,000 tonnes per year.

The Institute is also actively engaged in expediting the setting up of the following potassium fertilizer plants: (i) potassium chloride in two or three marine salt works, (ii) potassium schoenite from rest of the marine salt works.

[Salt Research & Industry, 3 (1966), 1, 1-2]

Pool Issue Prices of Imported CAN

The pool issue price of imported calcium ammonium nitrate of 26 per nitrogen grade for supplying to state Government and union territories has been fixed by the Government of India as follows:

(a) Packed in jute bags as bags rebagged in jute over-bags—Rs. 405/te; (b) packed in paper bags—Rs. 405/te.

The above prices are per tonne gross, f. o. r. ports/despatching stations paid by Central Fertilizer Pool up to rail-head destination by the shortest route.

[Dept. of Agri., Union Ministry of Food, Agric., C.D. & Coop., Letter dt. 26.8.66.]

Desulphurization of Hydrocarbons by the OD Process

A new process for the removal of sulphur compounds from hydrocarbons has been developed by Dr. C. Otto Gmbh of Bochum and Degusa of Frankurt—Main.

Unlike the conventional hydrogenation process the new process uses no nickel or other catalyst, and hydrogenation in the presence of sodium monoxide is not carried out under pressure. Desulphurization is effected in the gaseous phase and in temperature range of 180-350°C.

The main reaction is represented as $2Na_2O + RSR = Na_2S + 2NaOR$. In theory 100 kg. of sodium oxide should remove 26 kg. of organically combined sulphur, but in practice only about 75% of the theoretical efficiency is obtained.

The OD process is considered to be of considerable value in the pretreatment of gases to be used for synthesis gas or town gas.

[Sulphur, No. 63, May 1966, p. 38]

New Phosphatic Fertilizers

(*i*) *Egypt:* Egyptian workers have reported on a new phosphatic fertilizer produced from basic slag, hydrochloric acid and phosphate rock.

The process employed involves the acidulation of phosphate rock with hydrochloric acid and neutralization of the resulting phosphoric acid mixture with basic slag, whereby the fertilizer is obtained as a precipitate, which is then filtered, washed and dried. The process is stated to improve the phosphorous availability of basic slag and promises to be of interest.

(*ii*) *W. Germany:* An aluminium-calcium phosphate containing 31% H_3PO_4 and a partly disintegrated calcium phosphate with 38-40% H_3PO_4 were compared on various soils with basic slag, superphosphates and Reno natural phosphate. The former is only suitable on calcareous soils and had a similar effectiveness to basic slag. The latter was comparable with superphosphate.

[Phosphorus and Potassium, No. 21, Feb., 1966, p. 42]

New Process for Potassium Sulphate

In a two stage process developed by Saskatchewan Research Council, potassium sulphate of 95% purity is produced by a reaction between potassium chloride and a mixture of sodium and magnesium sulphates. The process is an attractive one since magnesium chloride and sodium sulphate are produced by recirculating the brines, while potassium chloride can be recovered from the brine circuit. The success of the process depends on the removal of sodium compounds from the brine in the first stage and the removal of magnesium compounds from the brine in the second stage.

[Phosphorus & Potassium, No. 21, Feb,, 1966, p. 41]

Losses of Nigrogen by Ammonia Volatilization from Surface Fertilized Tropical Forest Soils

Losses by ammonia volatilization from nitrogen fertilizers applied to six tropical forest soils have been studied. A micro-diffusion technique was used to measure the losses and to investigate the effects on these losses of soil pH, temperature, drying, amount of soil water, cation exchange capacity, fertilizer placement and soil sterilization. Volatalization increased when soil pH, temperature and drying increased; it was also greatest from soils with small cation exchange capacity. Nitrogen losses were decreased by burying the fertilizer in the soil, sterilizing the soil and by adjusting soil moisture above and below 25% water holding capacity.

[Acquaye, D. K. and Cunningham, R. K., Trop. Agriculture, Trin, 1965, 42 (4) 281-291, Abstr., NPKS Abstract, Vol. 53, May 1966, p. 8]

Liquid Fertilizer 11-37-0

Using wet-process phosphoric acid, allied Chemical Corp. has started its first commercial production of 11-37-0 liquid fertilizer. The 11-37-0 ammonium polyphosphates solution is the most recent development in higher analysis materials, development of which was begun by T.V.A. in 1958 when an 11-33-0 fertilizer material was introduced and the present fertilizer is the development of that fertilizer.

[Phosphorus & Potassium, No. 22, April/May 1966, p. 49]

Slow release fertilizers

On the occasion of the Annual Convention of the National Plant Food Institute of U.S.A. in June 1965, Dr. Hignett of Tenessee Valley Authority reported among others about slow release fertilizers.

Fertilizers that release plant nutrients throughout the growing season or longer are attracting increasing attention. Potential advantages of slow release nitrogen fertilizer are increased efficiency of uptake by plants, minimizing gaseous and leaching losses, reducing application costs, and preventing burning of vegetation or damage to seedlings.

This is an impressive list of potential advantages. Probably no more than half

of the fertilizer nitrogen used in agriculture is utilized by crops as an average, so improved utilization would be an important advantage. To determine whether a slow release nitrogen material would be more effective, dozens of nitrogen compounds of varying solubility and chemical characteristics have been tested in the greenhouse and in the field. To date, there has been little indication that improved recovery of nitrogen by crops or increased long- or short-term yield can be attained through the use of slow release nitrogen fertilizers. On the contrary, the slow release materials were often inferior to rapidly available ones. The same general conclusion applied to phosphorus and potassium materials.

On the basis of results available it may be concluded that there are scant prospects of finding a slow release material that will improve nitrogen utilization in most agricultural situations, regardless of cost. However, the potential advantages are great enough to warrant continued research. Even though utilization may not be improved through slow release materials, there are other advantages that make these materials attractive for the increasing market in horticulture, home gardening, and turf maintenance.

[I.F.C. Vol. VII/6-June 1966]

Kampka-Nitro Process for Compound Fertilizers

The "Kampka-Nitro" process is stated to be a further development of the Odda process though both the processes belong to the wet process for the manufacture of compound fertilizers. The General Scheme of the Kampka-Nitro process, its advantages, process economics have been dealt with and compared with the Odda process.

As for the design development it is stated that the cooling of the reaction slurry takes place in stages. If those stages are precisely managed, a coarse, crystalline calcium nitrate-tetrahydrate is produced. As a result, the mother liquor can be easily separated from the salt by centrifuging. A comparative reduction in the required number of centrifuges can be achieved. Cooling is fully automated. The control system regulates the course of the individual cooling stages and the intervals for cleaning the cooling surfaces.

For the ammoniation-carbonation of the calcium nitrate, a special apparatus has been developed in which the Calcium carbonate can be precipitated in easily filterable form.

[Phosphorus & Potassium, Feb. 1966]

Reforming Process

Esso Research & Engineering Co., U.S.A. has developed a process for minimising the sulphur content in naphtha by using a hydrofining zone employing cobalt oxide and molybdenum oxide on alumina and a hydroforming zone employing platinum on alumina (Brit. Pat. 1027, 364).

The preheated naphtha feed enters the hydrofining zone to raise its temperature to between 450° and 510°C without passing the hydroforming zone. Next the temperature of the napththa fed to the hydrofiner is raised to 150°C and the effluent fed to the hydroformer after it has reached temperature.

The resulting hydrogen gas is separated and collected from the hydroformer effluent. Some of this hydrogen is recycled to the hydroformer.

Reaction continues until there is sufficient hydrogen-containing gas available for the hydroforming zone, and only then is a portion passed to the hydrofiner.

This is followed by activating the cobalt oxide-molybdenum oxide on alumina by adding carbon disulphide to the naphtha feed going to the hydrofiner. This converts metal compounds to sulphides while still continuing to supply hydrogen-containing gas to the hydrofining zone.

Carbon disulphide equal to between 0.1 and 0.6 per cent of the naphtha feed is required in practice and should be contacted with the catalyst oxides at temperatures between 150° and 315°C.

[E.C.N., June 10, 1966]

Purifying Hydrocarbons

Sulphur impurities in light petroleum distillate may be reduced to very small amounts (less than 1 ppm). Carbon monoxide present in the hydrogenating gas used for the hydrodesulphurizing light distillates has an injurious effect on the removal of sulphur, but this can be remedied by promoting a hydrodesulphurization catalyst with nickel instead cobalt.

Thus in a process for reducing sulphur contamination in the distillate to 0.3 ppm, a vapour mixture with hydrogenating gas containing oxides of carbon is passed over molybdenum supported on alumina, with nickel as promoter and as result the sulphur is converted into hydrogen sulphide. The latter is subsequently removed from the treated distillate.

Treatment is carried out at between 250° and 450°C and at pressure of 10 to 25 atm., using a mixture of three parts by volume of hydrocarbons per part hydrogen. However, it is advisable to maintain an excess of hydrogen over and above that is required to react with unsaturate hydrocarbon, carbon monoxide and carbon dioxide in the mixture.

The reaction mixture entering the catalyst bed should contain between 1 and 12 volume vaporized light distillate per volume hydrogen, and is passed through the bed at 50-600 vol of vapour/hour/vol of catalyst space under saturated conditions at 16°C and 30 in Hg. pressure. (British Patent 1, 028 245, The Gas Council, U.K.).

[E.C.N., June 17, 1966, p. 48]

Extracting Nitrogen Oxides

Oxides of nitrogen normally associated with the production of nitric acid and other industrial processes such as pickling may be removed to yield a more profitable by-product than before by scrubbing with an aqueous suspension of calcium hydroxide.

Sufficient material to absorb all the gases is required, and yields a solution of calcium nitrate and calcium nitrate, having a nitrogen content of up to 50-65 g/l.

To this solution, up to 2.5 mole sulphuric acid is added for each three mole calcium nitrate. Calcium nitrate is oxidized, nitric oxide is evolved, and calcium sulphate is formed as a separable precipitate.

In practice, temperatures up to 55°C are recommended for the scrubbing (British Patent 1,026,946, Potasse et Engrais Chimiques S. A. France).

[E.C.N., June 17, 1966, p. 48]

Gas, Coal or Oil

There is a fierce competition between coal, oil and gas as a source of energy.

Lord Robens, Chairman of the National Coal Board, has pointed out that there is room for all that can be produced. The remotely controlled mine is now a reality, and the distribution of coal is so much rationalized that it is now possible to load ships at the rate of 5,000 tons/hr. He thinks that some of the newest pits should be in a position to offer coal at the same price as North Sea gas even if this were to come down to 3.5 d/therm envisaged by the Gas Board.

During the last ten years, the whole of the U.S. fuel scene has changed. The oil companies have first lost ground to natural gas and more recently to coal. Although coal has lost two of its traditional market, it has regained many industrial users. Overall consumption of coal has in fact risen by 38 per cent since 1954. There is now some very promising new techniques in the pipeline-production of petroleum from coal at half the cost of conventional methods.

[Science Newsletter, High Commission of India in London, July-Aug. 1966, 7-9]

Farming without the Plough

An idea which has been put up at the Royal Agricultural Show at Stoneleigh, Warwickshire, is to use a chemical to replace the plough. A new herbicide—a Parquet—has the useful property of being rapidly inactivated on contact with the soil. It can be used to kill grass and weeds with no risk of damage to new crops. The seed can be sown immediately after spraying. There is no need for a plough to break up the soil to get rid of the existing grass and weeds first.

In the same show, a 4 ft. long rice transplanter costing about £5 has been displayed, which can enable a 2-man team to do the work of fifty. The design of the transplanter—a wooden framework with a hopper to hold the rice plants—is simple and any carpenter should be able to make it. Lift the frame and pull a lever and five pairs of tongs dig into the hopper and pick out two or three plants each. Drop the frame, pull the lever again—the plants are put into the ground. Trials have already been conducted in Ceylon and Burma with encouraging results.

[*ibid*, 14-15]

Ammonium Nitrate Process Know-How for Licensing Rights Offered

The Soviet State Licensing authority, Licensingtorg, is offering Licensing rights for a process to produce granulated ammonium nitrate, based on the neutralization of weak acid with gaseous ammonia. The intermediate process of producing ammonium nitrate solution is fully automated and provision is also made for automation of other parts of the process. Full details are obtainable from Licensingtorg, 32-34 Smolena Kaya Sennaya, Moscow G. 200, U.S.S.R.

[Nitrogen, No. 41, May/June 1966, p. 43]

Problems Connected with Manufacture of Concentrated Nitric Acid

Nitric acid can be synthesized either by heterogeneous reaction in a cooler-condenser or by the combination of this process with a vapour-phase reaction occurring in a reaction chamber. Russian workers, headed by I. M. Kaganovski, state that at a pressures higher than 3 atm. it is possible to obtain a highly concentrated 65-70% acid. To achieve complete transformation of nitrogen oxides, obtained by catalytic oxidation of ammonia into nitric acid the process should be carried out with partial recirculation of the gases. (*ibid*]

Zeolites for Cleaning Synthesis Gas

Oxygen-containing compounds in the mixture of hydrogen and nitrogen for ammonia synthesis lead to poisoning of the ammonia synthesis catalyst hence the careful cleaning of the hydrogen/nitrogen mixture, including methanization.

Russian work has shown that it is possible to replace this step by absorption on zeolites. According to the report it has proved possible to clean 30,000 m^3. of a mixture of hydrogen and nitrogen with 1 m^3 of Ca_4 zeolite at a temperature of 25-35°C and 300 atm. in a once-through operation, carbon-monoxides and carbon dioxide are claimed to be removed completely. The new point of the gas is reduced to −65°C. When using zeolite only today a mixture of hydrogen and nitrogen, it is stated that 60,000 m^3 of gas can be dried with 1 m^3 zeolite, whereby the dew point is reduced from −45 to −60°C. [*ibid*].

STATISTICS

TABLE 1—PRODUCTION OF CALCIUM AMMONIUM NITRATE (CAN) AND CONSUMPTION OF RAW MATERIALS AT ROURKELA FERTILIZER PLANT

Sl. No.	Year	Raw Material Used		C.A.N. Production, tonnes
		Coke Oven Gas, 10^3 Nm^3	Limestone, tonnes	
1.	1962	N.A.	—	9,489
2.	1963	1,31,070	55,932	1,23,766
3.	1964	1,72,867	60,790	1,51,114
4.	1965	2,15,573	82,309	1,86,732

[Communication from Rourkela Plant Authorities]

N.A. means not available

N.B.: C.A.N. Production started on 25-11-1962

TABLE 2—ESTIMATED LOSSES TO CROPS IN THE FIELD IN INDIA

Crop	Average Loss %	Source
Foodgrains	15	Krishi Sansar, 1963, 1 (4)
Mustard and oil	51.6	Ind. Oilseeds J. 1960, 4 (3): 125-141
	71.5	
	87.9	
Fruits	25	Ind. Agri. Brief. 1957, 3rd Ed.
Paddy	29	West Bengal by one Insect, 'Entomology in India' 1964, p.
	12	93 Mysore State by one insect, 2nd All Ind. Rice Work Conf. Srinagar
	44.15	All pests, Ent. Ind., 1964, p. 93
	50-200 kg./acre	Andhra Pradesh Ind. J. Ent. 17, 1955 175-182
	25	Andhra Pradesh, Ento, Ind., 92-98, 1964
	1.1+10+7=18.1	All pests, Agri. Production in India, Burmah Shell, 1959.
Sorghum	32-38	All pests, Field assessment in rural areas of Mysore State by CFTRI.
Field Beans	40-75	All pests, Field assessment in rural areas of Mysore State by CFTRI.
All grains	15-20	All pests. Value of losses: Rs. 1000 crores, K. B. Lal, Bull No. 20, Nat. Inst. Sciences, p. 80, 1962.
All grains	25-30	(27 million tonnes) by Rats—IADP, Ford Foundation, 1965.

(Losses due to birds, monkeys and other non-insect pests have not been included. From these figures 25% seem to be an underestimate for field loss of paddy.)

[S. K. Majumdar & H. A. B. Parpia, Vijnan Karmee 18(1966), 4, 5-11]

TABLE 3—ESTIMATED DEPREDATION OF STORED FOODGRAINS DUE TO INSECTS

Commodity	Storage Period, months	Grains Damaged, Average %	Number of Samples
Jowar	3	7	108
	8	53	101
Wheat	3	3	88
	9	31	28
Field beans	2	6	48
	6	93	76
Black gram	2	5	51
	6	46	67
Bengal gram	3	8	29
	8	23	35

*Ref: Majumdar, S. K.—Food Needs & Resources, [Nat. Inst. Sci. Bull. No. 20]

[S. K. Majumdar & H. A. B. Parpia, Vijnan Karmee 18(1966), 4, 5-11]

TABLE 5—ESTIMATED AGGREGATE LOSSES OF FOOD GRAINS IN INDIA

	Minimum, %	Maximum, %
Field or pre-harvest	15	25
Post-harvest handling	3	5
Storage	10	15
Defective processing	3	5
Transport/Transit	4	5
Hotels and household	5	6
Total	40	61

[S. K. Majumdar & H. A. B. Parpia, Vijnan Karmee 18 (1966), 4, 5-11]

TABLE 4—PROGRESSIVE TOTAL DAMAGE OF WHEAT DURING STORAGE, %

Place	Variety	June	Aug.	Oct.	Dec.	Feb.	April
			Bag Storage				
Kakinara	Red	0.2	0.5	5.1	6.7	7.3	10.2
	White	0.3	1.1	1.6	2.2	4.7	4.5
Mukameh	Red	—	0.4	11.3	13.2	14.2	17.8
	White	—	0.2	17.7	22.4	25.5	31.5
Hapur	Red	—	0.4	8.5	11.0	11.7	14.6
	White	—	0.4	11.3	13.3	14.2	17.8
Manmad	Red	—	0.9	8.0	10.8	12.2	14.0
	White	—	0.1	5.4	7.1	8.4	—
Hyderabad	Red	—	—	—	—	—	—
	White	0.2	0.8	3.0	4.1	5.1	—
			Bulk Storage				
Kakinara	Red	—	—	—	—	—	—
	White	—	0.1	0.9	2.5	2.9	5.2
Mukameh	Red	—	0.8	4.0	7.3	8.5	11.9
	White	—	0.5	2.5	3.7	4.0	6.5
Hapur	Red	—	0.7	4.1	6.2	8.5	11.2
	White	—	0.8	4.8	7.6	8.6	10.3
Manmad	Red	—	0.4	4.5	7.2	8.4	10.2
	White	—	0.8	1.1	3.7	3.8	—
Hyderabad	Red	—	—	—	—	—	—
	White	—	—	0.9	1.5	2.1	—

(Data indicate that during first two months the losses remained within 1% while in subsequent months deterioration was extremely rapid reaching as high a figure as 31.5%)

[S. K. Majumdar & H. A. B. Parpia, Vijnan Karmee 18(1966), 4, 5-11]

TABLE 6—OUTLAYS IN 3RD & 4TH FIVE YEAR PLANS

(From Draft Outline of the 4th Plan)

(Rs. Crore)

Head of Development	Anticipated Outlay in the Third Plan					Outlay in the Fourth Plan				
	States	Union Territories	States & Union Territories	Centre	Total	States	Union Territories	States & Union Territories	Centre	Total
Agricultural Production	176	7	183	20	203	539	17	556	164	720
Soil Conservation	65	2	67	11	78	191	5	196	22	218
Total Agricultural Programme	637	20	657	78	735	159	50	1609	335	1944
Total Agriculture, C.D. & Cooperation	975	30	1005	98	1103	1918	60	1978	432	2410

The Fourth Five Year Plan has taken into account the gaps left over in the implementation of the Third Plan. With this plan it is hoped to carry the national economy forward towards the desired goal of self reliance. The highest priority will be given to all schedules of agricultural and industrial productions which will reduce imports and promote exports. The highest priority in Industrial development will be given to the production of fertilizers, insecticides and agricultural implements.

[Yojana, Sept. 4, 1966, p. 7]

TABLE 7—EUROPEAN CHEMICAL PRICES

Prices exclude local taxes except in the case of Germany and Holland Prices for Single Deliveries Only	USA	BELGIUM		FRANCE		GERMANY		HOLLAND		ITALY		UK	
	US Cents lb	Francs kg	US Cents lb.	Francs kg	US Cents lb.	DM kg	US Cents lb.	Fl kg	US Cents lb.	Lire kg	US Cents lb.	Pence lb	US Cents lb.
1	2	3		4		5		6		7		8	
Ammonia, 25-28% sq. soln. RTC	1.33	2.38	2.2	0.205	1.9	0.30	3.4	0.24	2.9	23	1.7	—	—
Ammonium sulphate, 21% N, 20 ton lots	1.60	2.73	2.5	0.293	2.7	0.23	2.6	—	—	36	2.6	2.00	2.3
Carbon dioxide, bulk liquid, 5-8 ton lots	—	8.50	7.7	—	—	—	—	—	—	80	5.8	3.25	3.8
Carbon dioxide, solid and liquid in cylinders, bulk purchase	2.50	9.50	8.7	—	—	0.45	5.1	—	—	90	6.5	4.50	5.3
Naphtha, 90/190, RTC [8.70 lb per gal.]	—	3.90	3.5	0.40	3.7	—	—	—	—	90	6.5	2.64+	3.1
Nitric acid, 100% basic, RTC	3.90	6.00	5.4	0.24	2.2	0.24	2.7	—	—	36	2.6	3.50	4.1
Phosphoric acid, food grade 75%, ton lots	5.60	11.00	10.0	1.00	9.2	0.83	9.4	0.75	9.5	147	10.7	9.50	11.1
Potassium nitrate, refined, 100 kg lots	9.50	7.00	7.4	0.75	6.9	1.76	20.0	—	—	105	7.6	6.80	8.0
Sulphuric acid, 66° Be, RTC	1.22	1.64	1.5	0.12	1.1	0.13	1.5	0.14	1.8	19	1.4	1.49	1.7
Superphosphate, bulk, 18% P_2O_5, 20 ton lots	0.86	1.34	1.2	0.111	1.0	0.17	1.9	—	—	20.5	1.5	1.51	1.7
Urea, 46% N, industrial, 5 ton lots	5.00	4.50	4.1	—	—	0.41	4.7	0.30	3.8	62	4.5	3.50	4.1

[European Chem. News, 10 (1966), 234, 12-18]

TABLE 8—NITROGENOUS FERTILIZERS CAPACITIES INSTALLED OR APPROVED DURING 4TH PLAN

(Target of production 2,000,000 tonnes of N.)

Name of the factory	Capacity in terms of nitrogen (Tonnes)	End-product and capacity, tonnes		Raw Material	Likely date of Completion
A. FACTORIES IN PRODUCTION					
I. *Public Sector*					
1. Sindri	117,000	Amm. Sulphate	355,000	Coke oven gas	
		Double Salt	121,920	Coke & Gypsum	
		Urea	23,470		
2. Nangal	80,000	Cal. Amm. Nitrate	388,000	Power	
3. Trombay	90,000	Urea	99,000	Naphtha/Refinery Gas	
		Nitrophosphate	330,000	Fuel	
				Oil.	
4. Rourkela	120,000	Cal. Amm. Nitrate	594,780	Coke Oven Gas	
5. FACT, Alwaye	70,000	Amm. Sulphate	200,000	Electric power and	
		Amm. Phosphate	135,000	Naphtha	
		Amm. Chloride	25,000		
6. Neyveli	70,000	Urea	154,000	Lignite	
7. Belagula	1,300	Amm. Sulphate	6,710	Power	
	548,300				
II. *Private Sector*					
1. Ennore	8,000	Amm. Phosphate	52,830	Naphtha	
2. Varanasi	10,000	Amm. Chloride	40,640	Coke	
	18,000				
III. *By-product from coke oven plant (Public/Private)*					
By-product from Coke-oven plant	20,000	Amm. Sulphate	100,000		
Total A:	586,300				
B. PROJECT UNDER IMPLEMENTATION					
I. *Public Sector*					
1. Namrup	45,000	Urea	55,000	Natural Gas	Aug. '67
		Ammonium Sulphate	100,000		
2. Gorakhpur	80,000	Urea	179,320	Naphtha	Dec. '67

Name of the factory	Capacity in nitrogen (Tonnes)	End-product and capacity, tonnes		Raw Material	Likely date of Completion
3. Durgapur	145,000	Urea	305,000	Naphtha	March '69
4. Cochin	145,000	Urea	330,000	Naphtha	March '69
5. Madras	190,000	Com. fertilizers	550,000	Naphtha	March '69
		Urea	54,600		
Total	605,000				
II. *Private Sector*					
1. Visakhapatnam	80,000	Amm. Phosphate	365,000	Naphtha	July '67
		Urea	16,500		
2. Gujarat	96,000	Urea	100,000	Naphtha Refinery Gas	Aug. '67
		Amm. Sulphate Phosphate	256,000		
3. Kanpur	200,000	Urea	450,000	Naphtha	Mar. '69
4. Ennore Expan.	8,000	Amm. Sulphate	38,610	Naphtha	Oct. '68
Total	384,000				
Total B	989,000				
Total A & B	1,575,300				
C. PROJECTS APPROVED IN PRINCIPLE					
I. *Public Sector*					
1. FACT IV Stage Expan.	22,000	Change in composition of Amm. Phosphate 16: 20 to 20 : 20		Naphtha	Mar. '69
Total	22,000				
II. *Private Sector*					
1. Goa	160,000	Urea	340,000	Naphtha	Mar. '69
2. Kota (DCM)	130,000	Urea	240,000	Naphtha	Mar. '69
		Diamm. phosphate	60,000		
3. Kothagudam	61,500	Urea	100,000	Naphtha	Early '70
4. Mangalore	220,000	Urea	115,000	Naphtha	Jan. '70
		Complex Fertilizer			
		Calcium Amm. Nitrate			
5. Gujarat Expan.	92,000	Urea	200,000	Naphtha	Jan. '70
Total	663,500				
Total C	685,500				
Total (A, B & C)	2,260,800				
D. PROJECTS PROPOSED FOR IMPLEMENTATION					
I. *Public Sector*					
1. Trombay Expan.	113,000	Urea	211,250	Naphtha	Dec. '69
2. Haldia	200,000	To be decided		Naphtha	Dec. '70
	313,000				
Total A to D	2,573,800				

[Based on Data Collected by the Union Ministry of Petroleum & Chemicals, Govt. of India]

TABLE 9—COMPARISON OF PRODUCTION COST OF SULPHURIC ACID FROM SULPHUR, PYRITES, GYPSUM (REDUCTION PROCESS) AND ANHYDRITE (CEMENT ROUTE)

Production basis: 50 Tonnes sulphuric acid per day

Capital required (Lakhs)	Sulphur	Pyrites	Gypsum	Anhydrite
	14	33	35	50

Cost Items	Unit	Rate Rs.	Quantity required				Cost			
			Sulphur	Pyrites	Gypsum	Anhydrite	Sulphur	Pyrites	Gypsum	Anhydrite
(A) FIXED EXPENSES/TON										
Sulphur	Rs. per ton	300	0.35	—	—	—	105	—	—	—
Pyrites	,,	53	—	0.93	—	—	—	49.5	—	—
Gypsum (mine head)	,,	12	—	—	2.3	—	—	—	27.5	—
Anhydrate (mine head)	,,	15	—	—	—	1.8	—	—	—	27
Power	kWhr	.08	65	144	120	300	5.2	9.1	9.6	24
Cooling water	% gal.	0.4	440	3300	1000	3600	0.17	1.32	0.4	1.44
Boiler feed water	,,	0.6	180	180	180	180	0.11	0.11	0.11	0.11
Fuel oil	Gal.	0.07	—	—	25	32	—	—	24.25	31.04
Shale (as quarried)	tons	15	—	—	—	0.36	—	—	—	5.0
Coke	,,	70	—	—	—	0.15	—	—	—	10.5
Coal	,,	48	—	—	—	0.25	—	—	—	12.00
Catalyst provision	,,	—	—	—	—	—	1.0	1.5	1.5	1.5
Total A/Ton							111.5	61.5	63.3	113.5
(B) FIXED EXPENSES/MONTH										
Salaries & wages							7,700	12,500	12,700	14,000
Repairs & maintenance		(3% of capital)					3,500	8,300	8,800	12,200
Depreciation		(10% in M/c.)					10,700	26,700	28,300	41,300
Interest		(7% on working capital)					2,700	500	300	1,000
Insurance		(1%)					1,500	2,800	3,000	4,200
Total B							26,100	50,800	53,100	72,700
Cost B/ton							17.3	33.8	35.5	48.4
Total Cost/ton (A+B)							128.78	95.3	98.8	161.9
(C) CREDITS										
Steam							14.5	14.5	14.5	14.5
Lime or Clinker				Fe_2O_3 no credit	0.75	1.04	—	—	45	30
Total Credit							14.5	14.5	59.5	44.5
Net Cost/ton							114.28	80.83	39.36	117.4

Note: In cost computation, other expenses like factory overheads, administration, sales and purchase organisations are common for the four raw materials and have not been considered.

Gypsum and anhydrite price is at mine-head. Break even freight can be calculated to match the cost of production from sulphur. Pyrites cost includes rail freight for about 800 km.

[N. K. Mehra, Indian Chem. J., 1(1966), 2, 35]

Explanation of Some Physico-Optic Phenomena in the Light of the Theory of Universal Spherical Wave of the "Energy Field of the Universe and Atom"

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The equilibrium configuration of the Universal Spherical wave of the energy field, described in the works "Energy Field of the Universe and Atom", Parts I & II and "Introduction to Understanding of the Theory of Universal Spherical Wave of the Energy Field of the Universe and Atom" should prove to be, a unified field concept capable of explaining almost all self-sufficient equilibrium phenomena having isolated existence. In the present article it is intended to apply the same theory to explain some of the physico-optic phenomena.

The concept of energy, as space associated with energy radiation and emission of light of different colours, is explained and it is shown that any light radiation must have a certain magnitude of space of its configuration depending on the intensity of the radiating source of light. It has been explained by diagramatic presentations as to how the apparent course of light, emanating from a source, passing an observer fixed in space, would be observed as being deflected towards or away from the observer. The amount of deflection would depend on the intensity of the radiation at a fixed position, the magnitude of space through which the radiation would pass and the position of the observer. This would explain the apparent appearance of the orbit of Mercury as an ellipse, the shift of the perihelion of Mercury with time, the Doppler's effect as change of frequency and wave length when the source of light and the observers are in relative motion, red shift and bending of light radiation from distant stars, while passing through space near an object, like the Sun.

All sources emitting coloured radiation have a magnitude of space associated with them which is responsible for the observation of the object at an apparent location which is invariably different from its actual location.

The tetrahedral configurational manifestation of universal spherical wave, due to a fundamental dimension like energy, implies that the fundamental dimension, which in its original state before manifestation occurs, assumes position of centre of imaginary four positions of tetrahedral configuration, in that purest state of existence has no association with derived dimension like matter in the four positions of its configuration. Configuration associated with the fundamental in its infinitely pure state of concept has only imaginary tetrahedral positions of nil magnitude of size of configuration. In the subsequent actual manifestations, the positions associate derived dimension starting with least intensity in those positions which progressively manifest and develop with increasing magnitude of variability, increasing size of configuration and also in magnitude of intensity of derived dimension associated with the positions. As cause of this process, the intensity of the fundamental dimension is responsible for creating the configuration from nil magnitude of its size from a central point of position. As the size of configuration increases, the spherical surface, generated by the positions associating with increasing magnitudes of variability, also increases. The bigger the magnitudes of the generated surfaces, (i.e. the bigger the radial distance from the centre), the less becomes the intensity of the emanating fundamental dimension. Surfaces are generated by orbital time in configuration,

described by the positions in association with the dimension of variability. The spherical space or sphere is generated by radial space and orbital time in association with variability of the positions.

The significant point which requires to be understood is how the source at the centre and the emanating sphere would appear in perception to an observer. The four positions of the tetrahedron, varying in magnitude, contain matter significance of varying intensity associated with energy intensity in inverse ratio. Our perception of this manifestation occurs through material positions. Therefore, what will be perceived of the phenomenon is the magnitude of the spherical surface generated and the energy intensity associated with the surface. The higher the energy intensity associated with the surface, the less would be the magnitude of the spherical surface, i.e. the spherical surface will be nearer to the centre. If energy intensity increases to a point of position, the surface would progressively become less till it would no longer be perceptible since the fundamental dimension, which emanates the configuration, would reduce in size to nil, assumes a magnitude of intensity tending to infinity; in this state there is no association of matter intensity with the positions of the configuration and therefore the configuration of the fundamental dimension vanishes from perception.

As a general deduction from this, one can assume that if an emanating manifestation is observed from a position in space and time, the size of the configuration of the emanating radiation would depend on the intensity of radiation associated with its magnitude of spherical configuration. This, in other words, would suggest that the various radiating coloured light radiations would have different magnitudes of radial space association, depending on the intensity of energy association. A red radiation, which is less energy intensive, should show an equilibrium space association of radial magnitude higher than that of violet or blue which is higher energy intensive.

It is a matter of common experience that, in a city where various sign-boards for advertisement with different kinds of lights such as neon, helium, mercury vapour etc., are switched on in the evening, one sees that in the same sign board, if some letters are lighted by red lights they appear nearer to the observer than those which are lighted by green or blue lights. Conventionally, this phenomenon is attributed to various causes relating to the physiological properties of the eye such as the dazzling effect of light intensities on our visual organ. Indirectly, this could also be attempted

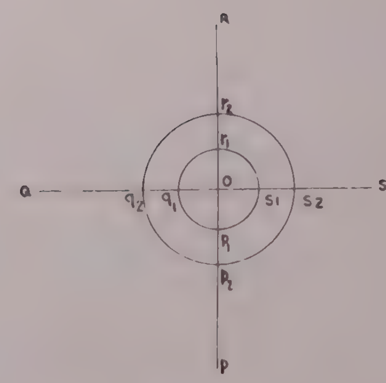

Fig. 1

to be explained by saying that this is nothing new since every colour, by virtue of possessing a different wave length, must have its own focal length when observed through the lens of an apparatus and red light has a different focal length from that of green or blue.

These explanations ignore some important characteristics of space viz. that energy (radiation) is space and that for different colours, having different wave lengths of propagation, their associated energy intensity of space and the magnitudes of space associated with the radiations are different. This is not revealed in these explanations. The associated magnitude of space of red, *it will be seen*, is greater than that of green or blue. But the associated energy intensity of red is less than that of blue. Through Fig. 1, a simple explanation can be offered to this phenomenon. O is a point of position of a light radiating source. P, Q, R and S are the positions of the observers. If the source of light is red at O, the magnitude of space associated with red colour (in terms of radius) would be indicated by a sphere having the radial magnitude of space as $Op_2=Oq_2=Os_2=Or_2$, such that the observer at P will see the apparent position of light source O at p_2. Observer at Q will observe from his direction, the position of the same at q_2. Thus from P, Q, R and S, the observer will see apparent positions of the source of the red (which is actually positioned at O, the centre), to be shifted to the spherical surface through $p_2q_2r_2s_2$, radius of which is the magnitude of space associated with red colour.

If O, the light source, would be, say, green, the corresponding apparent observed positions from P,Q,R,S would be a spherical surface passing through $p_1q_1r_1s_1$, radius of which is less than that of the former. Thus, it is not difficult to visualize why the red coloured letters in a lighted sign-board look nearer to the observer than those with lights emitting green or blue colour. When the importance and the effect thereof of such displace-

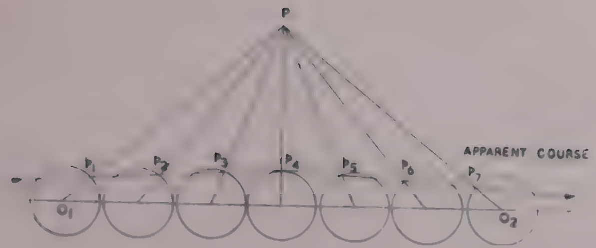

Fig. 2

ment of actual positions of the emitting source to the apparent positions by an observer are considered in the case of various astronomical objects like stars etc. in the context of the perceptible universe as a whole, these being observed from a point of position in the space and time continuum which itself is simultaneously undergoing change in position relative to those objects, the amount of complication, which would be involved in determining the actual course described versus their apparent observed course, must indeed be enormous. This single factor would be responsible for the observed course of orbit of Mercury as elliptical having major and minor axes, instead of a circular orbit. This will be discussed in a subsequent section.

In the following the reasons why, to an observer situated at a point of position in space, a light radiation, actually describing a straight course, will appear to be deflected away from or bent towards his position have been discussed. Take Fig. 2. P is the position of an observer. O_1O_2 is the actual straight course of a light radiation. If the source of light has associated with it a constant magnitude of space indicated by the circles, then, while the light source describes the path from O_1 to O_2, the apparent course of the observed positions of the light source would be indicated by P_1, P_2, P_3, P_4, P_5, etc., a course which is bent towards the position of the observer. The apparent position of the course is most bent from the straight course at P_4 and least at P_1 and P_7 etc. Although the light source would be describing the straight path relative to the point of position of the observer, the apparent observed course followed by the source would appear to be bending towards the position of the observer. It may be noted that the bending effect will be higher for the source emitting light associated with greater magnitude of space. The source, associated with less magnitude of space, will exhibit less bending towards the position of the observer. If the light has least magnitude of space associated with it, the observed course would be nearest to the straight path O_1O_2.

Now, take Fig. 2(a) in which the observer takes up position of E at a radiating source of energy of high intensity like the Sun. The magnitude of space, due

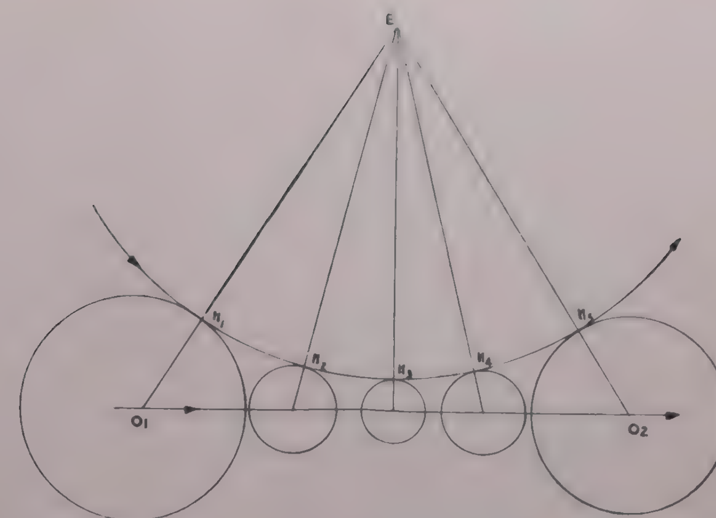

Fig. 2(a)

to energy radiation of the source, will increase radially with corresponding decrease of energy intensity in the space. Now suppose a radiation, having certain magnitude of space associated at O_1 and its centre, describes a straight course O_1O_2: the apparent observed course described by this radiation would be n_1, n_2, n_3, n_4, n_5, n_6 etc. The radiation having higher space magnitude at O_1, will progressively vary in its magnitude as shown in Fig. 2(a). During its propagation the radiation will be decreased in its associated magnitude of space till it arrives at the least magnitude nearest to the observer after which again it would increase in space magnitude till it arrives at O_2. The net result is that the observer at E will see the radiation describing a bent course and not a straight one while passing by his position situated in space of high intensity of energy. The general principle of the bending of light, while passing near an object emitting high energy intensity of radiation like the Sun, can be explained on this basis, together with other equipotential effects which will be described later while explaining the phenomenon of bending of light.

In Fig. 2(b), a case is considered [just the opposite of Fig. 2(a)], in which M is the position of an observer

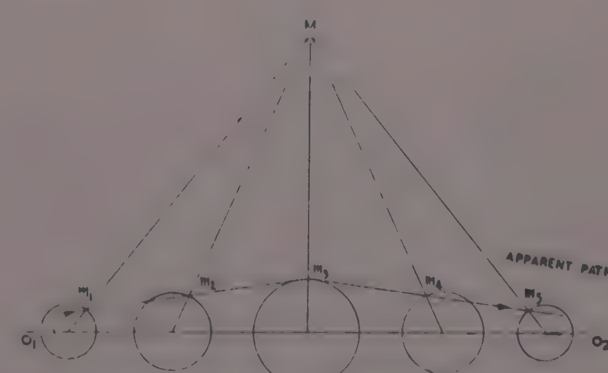

Fig. 2(b)

situated in a field of high magnitude of space, i.e. the intensity of energy in space in its vicinity is low. Suppose a radiation of higher energy intensity (i.e. with lower associated magnitude of space) passes by M, in which its centre would describe a straight line. In these conditions, as the radiation approaches M, its magnitude of space increases till it is highest at the point nearest to M. Thus, the apparent path of the beam wolud be m_1, m_2, m_3.... deflected towards the observer.

The cases, which have been described in Figs. 2, 2(a), 2(b), are hypothetical; in 2 it is assumed that the magnitude of space associated with the radiation passing by the observer with its centre describing a straight line is not encountering varying magnitudes of space while describing the path and the radiation is maintaining its constant magnitude of associated space. Field space near the observer and the radiation passing in space are not interfering with each other as shown in Fig. 2. In Fig. 2(a), the observer is situated at a position of space of high intensity of energy which has created a field space with increasing magnitude of space radially outward and another radiation, having bigger magnitude of space associated with it than the position of the space of the observer, passes through encountering, during the course of propagation, varying magnitudes of space. In the third case [Fig. 2(b)], the observer is situated at a position in space of high magnitude, i.e. in less intensive space and a radiation is propagated near it initially with higher intensive space. A radiation of higher intensive energy, i.e. associated with lower magnitude of space, encounters varying magnitudes of space while passing by the observer, the mechanism being the opposite of that case in Fig. 2(a).

It has been assumed in the above figures that during the propagation, the radiating sources are only encountering pure space, although containing varying magnitude of energy intensity. The space may contain additional entities like a gaseous atmosphere of radially decreasing concentration from an observer as M in Fig. 2(b) and the apparent course of path of the source perceived by the observer would further be modified by the interaction of energy between the radiating source and the material medium constituting the gaseous atmosphere. The effect would, in Fig. 2(b), be that the radiating source would have accelerated increase of space magnitude as the source would be nearer to the observer, i.e. the deflection towards the observer would be more than when there was no gaseous atmosphere.

Phenomenon of Doppler's Effect

Doppler's effect is generally reckoned as the observed difference between the frequency of the wave generated by a source and the frequency which is perceived by an observer when they are in relative motion.

However, the source generating wave and the observer may be stationary with respect to each other in the field of observation or they may be moving, relative to each other, in the field of observation. In the former case, the phenomenon cannot be likened to Doppler's effect. When the source and the observer are positioned in different places and are stationary, the frequency of the light emitted by the source is not equal to the frequency detected by the observer. The observer will experience a frequency lower than that of the source and thus record a shift of wave length (towards red). If, however, the observer keeps on moving along the constant spherical wave front, generated by the source, he will experience no change of frequency, though there is still a relative motion between the source and the observer. The source, generating the radiation wave from a point of position in a field, must have a higher intensity of the property which is being propagated in the form of wave, be it of sound or light. It may be energy as space (which is conventionally called vacuum) or it may be sound in a gaseous space.

Let O (Fig. 3) be the point of position in space of highest intensity of a wave emanating source of radiation or sound, being propagated in space (Fig. 3 is a diagram of this phenomenon projected on a plane of paper). Conventionally, O is the position of energy having the highest frequency and the least wave length or, in the other words, least

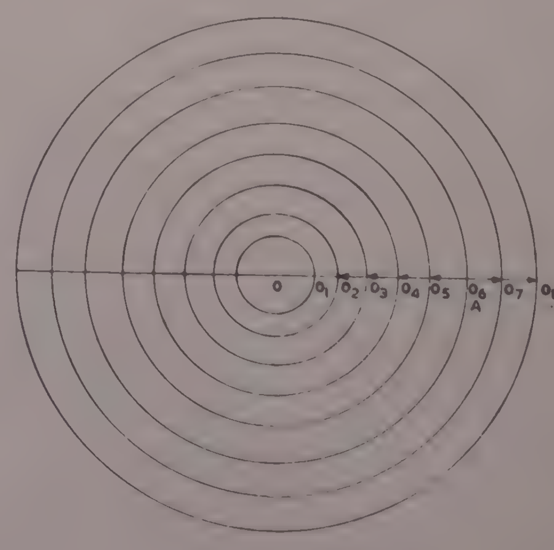

Fig. 3

magnitude of associated space. The propagating waves of energy generate O_1, O_2, O_3, O_4 magnitudes of wave length at increasing radial distances from the source, having decreasing intensities of energy and with correspondingly decreasing frequencies. An observer A, situated in space field in which the waves have been set up due to the source O, will receive the wave characteristics corresponding to O_6 having a frequency progressively reduced radially from O towards OA. The intensity of energy associated with the wave is progressively less radially towards OA and the frequency is also less following the same pattern, but the magnitude of space (which corresponds to wave length) is of an increasing order towards OA. In this field, if A recedes radially towards positions away from O, while the position of O is stationary with respect to A in the field, A will experience wave characteristics O_7, O_8 having further reduced frequency and energy intensity but with higher magnitude of space (i.e. wave length) etc. If A would move towards O, the observer will progressively experience O_5, O_4, O_3 etc. waves of decreasing magnitudes of space (i.e. lower wave length).

Now suppose the observer is stationary in the field and the wave generating source O moves towards A. The corresponding wave fronts O_1, O_2, O_3, O_4, O_5 will progressively meet the observer depending on the speed of O towards A. Similarly, if the generating source O moves away from A, the wave fronts at A, viz. O_6 will progressively be converted into O_7, O_8 having corresponding properties; at any instant, perception of these by A will again depend on the speed of O relative to A.

The general discussion referring to Fig. 3 in the above would lead to the following conclusions: *If an observer could, by some means, move towards an energy emitting source like sun, associated with space of high intensity of energy and low magnitude of space, he would experience in perception during motion increasing energy intensity and increasing frequency of the radiation wave and decrease in the associated space magnitude of the wave.*

Elliptical Orbit of Mercury

Let us now, applying the above concepts, try to explain the observed elliptical orbit of Mercury. Before doing so, it is necessary to recapitulate the configuration of the system of planets and orbits with respect to the Sun in the light of the present theory as was explained in "Energy Field of the Universe and Atom", Part II, Chapter 9, Page 242.

In Fig. 4, S is the position of the Sun. It occupies the apex of a cone of its radiation field along the surface of which all the planets at various radial distances describe approximately circular orbits. Assume that M is the circular orbit of Mercury, V of Venus, E of Earth, M_1 of Mars and so on. Suppose SX is the axis of the cone. Looking from X, the orbits (in Fig. 5), would all appear on the plane of paper to be concentric circles with the Sun at the centre. In Fig. 5, only the orbits of Mercury and Earth have been shown. Mercury reflects light of certain wave length, i.e. of certain magnitude of space associated with it. Suppose the magnitude of space associated with Mercury light is shown by circles with centre positions at p,q,r and O as shown in Fig. 5. With respect to the position of earth fixed at E, the apparent orbit of Mercury would appear to pass through p_1 q_1 r_1 o_1 etc. It would be seen that the observed position p_1 is nearer to earth than its actual position in Mercury orbit at p. Similarly, the observed position at r_1 is nearer to the earth while the actual position of Mercury is at r. The distance q_1o_1 is less than qso. Thus the described course passing through p_1 q_1 r_1 and o_1 would be that of an ellipse, r_1p_1 being the major axis and q_1o_1 the minor axis. The position r_1 is the perihelion of Mercury and the position p_1 is its aphelion with respect to the Sun. Though this purely qualitative picture of the apparent elliptical orbit of Mercury round the Sun has been arrived at from the simplified figurative projected configuration of the solar system on the plane of paper, taking the configuration of Fig. 4 as a whole in conventional three-dimensional space with certain space magnitude associated with the light of Mercury, the resulting figure will also depict similar observed elliptical orbit and not a circular orbit from any other position of earth in its orbit.

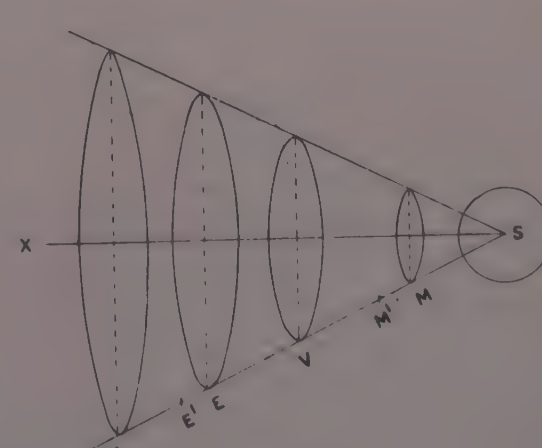

Fig. 4

Perihelion Shift

So long as the earth E maintains constancy of orbit with respect to time and so also Mercury, the relative elliptical orbit of Mercury with respect to E and S will remain the same. But the solar system is expanding with time. The planets, with respect to the Sun, have been shown in Fig. 4 as describing complete circular orbits along the surface of a cone, but actually, with the progress of time, each planet describes spiral form of orbit and not strictly circular orbit. Though their shift with respect to time is very small in our perception, nevertheless, it should be something finite and positive. It may not be appreciable in a year but say, after a century or so it will be. Thus, after a certain lapse of time, say, a century, the position of the orbit of Mercury in Fig. 5 would be shifted to position, say M′ and E would then correspondingly be shifted to describe orbit at E′. In Fig. 5, the positions of Mercury perihelion and aphelion and Earth, as they should appear on the plane of paper, after a century relative to the previous positions are shown at r_2 and p_2 respectively.

The magnitude of the associated orbit of mercury with new position will be higher than that of previous orbit. It may be observed that in the new elliptical orbital course of Mercury, the perihelion will take up a new orbital position through, say, r_2, which, with respect to the previous alignment of earth, the Sun and the perihelion r_1, will now have a new alignment through new positions of Sun, Earth and Mercury which are E′, p_2, r_2 etc. The angular shift is indicated in the figure by a°.

Shift of Spectral Lines (Red Shift)

In Fig. 2(a) it was shown that, when a radiation, having certain magnitude of space associated with it which is higher than that of another radiating source situated at E having higher energy intensity or space intensity, is forced to pass through space close to the higher energy intensive source E, the space magnitude of the former would progressively reduce till it is least when the radiation is nearest to E, viz. n_3 in Fig. 2(a). Similarly, when the radiating source, radiating from a position in space of higher energy intensity, propagates through space, having lower intensity of space and energy, the radiation would progressively associate bigger magnitude of space, as shown in Fig. 2(b). This shows that a radiation, from a source of higher intensive energy, creating a wave due to vibration having higher frequency and lower wave length i.e. with less magnitude of associated space, propagates radiation, associating radially with increasing magnitudes of space and decreasing magnitudes of frequency. The phenomenon would be observed when the radiation will be received and the apparatus, while receiving the radiation situated in a space of higher magnitude of space, will record a frequency lower than that of the source and a longer wave length. The red-shift, as explained in this mechanism, occurs in a field medium in which only space-energy is present and no material medium (like that of atmosphere) is present in space through which the radiation has to pass. The phenomenon would be somewhat similar to the phenomenon of Doppler's effect. But, if the observation would be made on the surface of planet like earth which is surrounded by its own gaseous medium distributed in space surrounding it (to a considerable radial height) and a radiation from a high energy intensive source, having high intensity of space passing through space devoid of material medium is incident on earth's surface. The radiation, before being observed on the surface of earth, has to encounter the material medium also. Therefore, as explained in Fig. 2(b), the radiation from a higher energy intensive space progressively develops its increasing magnitudes of associated space, but, in addition, the material medium will have a further effect on changing the magnitude of associated space of the radiation Therefore, when such a radiation, from a highly intensive energy source, would be made to propagate towards less energy intensive space and be received by an observer, he will receive, if there is no material medium intervening, certain frequency which is lower than energy frequency of the source; in addition, if the radiation will have to encounter the material medium or atmosphere, due to further absorption of energy by matter, the associated space magnitude of the radiation will be further increased (in other words, the associated space will have less energy intensity) and have lower frequency and greater shift towards the red end of the spectrum.

Bending of Light in So-called Gravitational Field While Passing by an Object like the Sun

While discussing the problem in the light of the present theory, the various terminologies employed in it should not be mixed up with the corresponding interpretations of modern scientific terminologies in their specific and separate perspective. For example, this phenomenon is sometimes expressed as bending of a ray of light due to "gravitational field". Parallelism or difference between "gravitational field" in the prin-

ciple of relativity and the concept of energy space field of varying intensity of energy in the present theory requires clear understanding. The difficulty lies in the contradictory, if not anomalous, significance of relativistic gravitational field when applied to both the space field near the Sun (which is energy intensive) and the space surrounding a celestial massive object (matter intensive and not energy intensive) like Saturn or Jupiter, both being termed "strong gravitational" field. What is intended to be brought out is that the conventional gravitation or gravitational field and their significance, vis-a-vis relative matter positions in space as such is not clear. For example, when a volume of certain material gas is cooled it means that the energy as space, which separated the molecules in the volume of the gas, has been removed by some means and the matter positions in gas would tend to reduce to a point. This is gravitation, but this gravitation of matter positions is taking place in the absence of energy which was responsible for keeping the matter positions apart.

There is another kind of gravitation which can also be considered and that is to take a volume of gas and to apply constraints on it such that the whole volume along with the space is reduced to a point of position. This would mean that the matter positions have been forced to collapse along with the space, i.e. energy, as a result of which the matter positions along with the space have been converted into a state of high energy intensity or space intensity. This can also be construed as a case of gravitation of the matter positions; even the matter positions may be left out and merely the space of certain unit magnitude can be reduced to a point of position. The intensity of space energy would thus increase or decrease. Therefore, while considering the word gravitation or gravitational field, differentiation is necessary as to *what is being gravitated*? Is it matter positions in space gravitating to a point in absence of space energy or the space itself gravitating towards a point of higher intensity? This point must be made very clear. In the present theory the space is the energy field. The higher the intensity of space, the higher is the energy intensity; the bigger the unit magnitude of space in configuration, the less is the space intensity or energy intensity.

It would thus be clear that the space nearest to the Sun is highly space intensive (energy intensive). The relative unit magnitude of space is small compared to the space that would be obtained near a planet like Saturn which is situated far away from the Sun. The relative unit magnitude of space near Saturn is thus much higher and the space intensity, i.e. energy intensity is correspondingly less. The gravitation of matter positions in space near Saturn would therefore be much greater, whereas near the Sun any energy radiation lower than the intensity of energy of the surface of the Sun would be brought closer to the Sun and its energy intensity would tend to increase, i.e. the original relative magnitude of space associated with the original radiation will be decreased in order to be in equilibrium with the field near the Sun. Thus, the unit magnitude of space associated with the radiation would be reduced which signifies that the radiation would gravitate towards the Sun.

The difference between the two cases is also shown by the following example: if the matter positions, undergoing gravitational changes near the Saturn's field, would be brought to the surface of the Sun, they would be repelled from the Sun's surface unlike energy (space) gravitation towards the Sun's surface.

In the two concepts, the directions of action towards the point or away from it have to be understood clearly. In the case of low energy intensive space, as is found near highly massive objects, gravitating towards any position, the space in between must be required to be removed and this process is conventionally termed as cooling or removal of the energy from inbetween the matter positions. The direction of matter position is towards a point whereas the space as energy has its direction of action radially away from the point of position towards which the matter positions collapse. Exactly opposite would be the case in a high energy intensive space as is found near an object like the Sun. A radiation, having certain unit magnitude of space relatively higher than that obtained in the vicinity of the Sun, would be reduced in its magnitude of configuration which means that the radiation would be attracted towards the Sun, signifying 'gravitation' towards the Sun, whereas if the radiation is associated with the heavy matter positions, which cannot exist in the vicinity of the Sun, it will undergo explosion or in other words repulsion from the vicinity of the Sun. Thus the direction of action of energy radiation in the vicinity of the Sun is towards the Sun whereas 'matter' would have to be repelled from the Sun's field. It is also conventionally understood that a strong gravitational field's opposite is the terrestrial atmosphere which is a weak gravitational field. This is difficult to reconcile in the light of the present theory. According to this theory, the surrounding space nearest to the Sun has high energy intensity or high space activity like gravitation. The space at a radial distance, further away

from Sun, is of lower intensity of energy and space. The space, in which a massive object would be situated and with which it would be in equilibrium, will have a bigger magnitude of space which must be less energy intensive and correspondingly lower space intensive.

If, therefore, the space near the Sun would possess high magnitude of "strength of gravitation", the same should be equivalent in meaning or significance in the present theory for a space field of high energy intensity or high space intensity. The significance of both appears to be the same. Similarly, the space surrounding a massive object, with which the latter may be in equilibrium, must be low energy intensive, low space intensive and of bigger magnitude of configurational space. These connote a different significance and should be equivalent to that of a field of a low gravitational strength in the conventional sense. If the significance of strength of space field in this theory, in terms of its energy intensity or space intensity, would correspond to the significance of gravitational strength of field as implied in relativity, it would have the opposite significance in field strength of space when its magnitude of size of configuration is taken into consideration. The magnitude of energy or space intensity is opposite to magnitude of size of configuration of space. The field, near an energy intensive object like the Sun, has high space or energy intensity and low magnitude of space configuration, but the field, near a massive object like Jupiter, is low energy intensive but of a high magnitude of space configuration. There is a great deal of difference in fundamentals between these two concepts. In the theory of relativity, mass and energy equivalence and inter-convertibility is the basis; but their relationship, in direction of action with magnitude of configurational space or space intensity, has not been defined. For example, it is not clear whether energy-matter equivalence retains identical significance when one is converted into the other or whether they assume functionally opposite characteristics in their direction of action when one is converted into the other. Does the strength of gravitational field lie in attraction or repulsion? If so, between what? Is it between two 'energies' or two 'matters' or between one energy and one matter object? Relativity does not clarify these questions.

In this theory, the two dimensions, matter and energy, have distinct but opposite significances. If one is action, the other is reaction. They may be equal but must be opposite in function so that the action of one counters the reaction of the other to maintain equilibrium. In the configuration of the spherical wave of the universal energy/matter field, as described in the previous works* the nature and functioning of the dimensions: energy, matter, space and time have been explained. *Space is the configurational container of energy and time is the configuration container of matter.* What is energy? The dimension energy in this theory is actually the intensity of space or force of space. The higher the configurational magnitude of space, the lower is the intensity of contained, i.e. energy. Similarly, the higher the configurational magnitude of time, the lower is the intensity of matter contained. The dimensions energy and matter manifest as intensity of space in configuration and intensity of time in configuration respectively. If space is of a lower magnitude in configuration, its intensity must be higher or in terms of energy the intensity of energy must be higher. Similarly, if the magnitude of time in configuration is low, the intensity time must be high, i.e. intensity of matter must be high. In considering energy, matter, space and time dimensions, constituting the wave configuration, magnitude of intensity of a configuration and magnitude of size of configuration are opposites. Action and reaction between these opposites generate and maintain equilibrium. Of the dimensions in the present theory, the one which creates field viz. energy, is the fundamental dimension and the rest are all derived. Energy creates space field while matter assuming position describes only time orbit in created field.

Comparing these fundamental concepts of the present theory with the 'gravitational field' concept in the postulates of relativity, it appears that gravitational strength of field corresponds to energy intensity of space. But the mention of the presence of strong gravitational field as identical for both the field near a massive object and the field of the Sun in relativity is not in agreement with the basic postulates of this theory in which the Sun is high energy intensive and low matter intensive, whereas just the reverse is the case with a massive object. The space near the Sun is high energy intensive in which matter intensity should be less for its equilibrium existence. In the solar system, matter in gravitational (attraction) equilibrium with the Sun is possible only when the matter entity is less massive and more energy intensive as in the vicinity of the Sun. Matter intensive bodies placed in highly intensive space near a high energy intensive object will undergo repulsion and not attraction. Therefore, in terms of gravitational attraction, matter objects in the field near the Sun would be strongly anti-matter and pro-energy and would be gravitationally attracted by virtue of energy potentials they possess (i.e. they

should be highly energy intensive in conformity with the intensity of space in which they would be placed). For the other kind of gravitational attraction of matter objects in space field, the latter should be anti-energy intensive and pro-matter intensive. For example, in the case of a gas, in which matter potentials are distributed in space of certain energy intensity, when the intervening space amongst the matter positions is removed by some means, say, by cooling, the matter positions would collapse by gravitational attraction to drops of liquid. It should be understood that in this case, the material objects, which are undergoing attraction towards one position, are situated in space having a weak gravitational strength of the field. Thus, in a weak space field, matter positions should have a tendency of collapsing to one position and energy in space should be removed or depleted or dispersed. On the other hand, matter positions should be repulsed or dispersed in a strong gravitational field and energy positions should be attracted to one another.

Accordingly, for a high energy intensive source at S, the varying magnitude of space, in order of increasing magnitude along one radial direction in which the emitted energy would be propagated, is shown in Fig. 4(a). The orbits s_1, s_2, s_3.... are all loci of increasing magnitudes of configurational space (size) decreasing in energy intensity (i.e. decreasing order of space intensity) in the field. The energy intensity has also been termed in this theory as energy potential. *Thus the orbits are in an energy potential gradient of space field of decreasing order of magnitudes from the source S.*

Before considering the details of the mechanism, first of all the nature of the radiation, which is to pass by the Sun, must be known. The characteristics of radiation source, its energy intensity, i.e. space intensity, corresponding frequency etc., relative to those of the Sun, should also be known. What would be the associated magnitude of space of the radiation having already described potential gradient or intensity gradient of space by its own energy radiation while entering the space field of the Sun?

The implications of the characteristics of the space field near a highly energy intensive source like the Sun may now be considered. An energy source like the Sun has its space field as in Fig. 4(a). in which the energy intensive source S occupies position as apex of cone of space field emanating in one direction creating increasing curved equipotential surfaces at radial distances with progressive increasing magnitude of space and decreasing energy intensities of space at the various surfaces. Figuratively, S_1, S_2, S_3.. etc. are shown as such curved surfaces in one direction of the Sun's field. If any source of energy, having identical properties as that of the Sun, would happen to be in its vicinity, it would occupy an identical position to the Sun i.e. it will be attracted to the Sun's position. Another object, having energy intensity corresponding to S_1, will find its position in the solar field along the curved surface S_1. Similarly, lower energy intensive objects would find their places in the space field due to the Sun along the various equipotential curved surfaces, depending on their energy potentials.

Now suppose an energy radiation from an outside source would be incident at A on the solar field with a magnitude of associated space, equal in the magnitude of space to an equipotential surface, say S_4 [Fig. 4(a)] through the point of incidence A; the radiation, while crossing the cone field, will travel along the spherical surface S_4 with the same magnitude of space associated with the original radiation. If, however, an original radiation, say, pA_1, prior to entering the field of the Sun, had a magnitude of associated space, bigger than the magnitude of space at the equipotential surface S_3 within the cone field passing through the point of incidence, say, A_1, the original radiation will be forced to assume higher intensity of space. The resultant magnitude of space associated with the radiation, while passing through the cone field through the point of incidence, will assume an intermediate magnitude (as at S'_3) of radius bigger than that of the curved surface S_3 through the point of incidence A_1. Thus the radiation, instead of crossing the cone field through the point of incidence A_1, will assume a course $B_1S^1_3$ with lower intensity of space associated with the radiation and with higher magnitude of space than that of A_1S_3. The course of the resultant radiation shifts from A_1S_3 to $B_1S'_3$ i.e. towards higher magnitude of associated space of resultant radiation passing through greater radial distance from the Sun. The apparent incident direction would appear to be along $P'B_1$ instead of pA_1.

Similarly, in the case of an outside radiation p_1A_2 incident at A_2, having smaller magnitude of associated space (i.e. higher energy intensity) than that of the magnitude of space associated with the equipotential surface S_5 through the point of incidence A_2, the resultant radiation, while crossing the cone field, would assume a magnitude of space intermediate between the magnitude of space of incident radiation p_1A_2 and the magnitude of space associated with the surface A_2S_5 and will follow a course, say, $B_2S'_5$ which is nearer to the Sun than A_2S_5. The resultant course will be shifted from A_2S_5 to $B_2S'_5$, giving appearance of incident

direction as P'_1B_2 instead of P_1A_2.

From the above, it would follow that if an incident radiation to solar space field has a bigger magnitude of associated space than that at the equipotential curved surface through the point of incidence, then the apparent direction of incidence and the actual course would be shifted away from the Sun and in the reverse case the apparent direction of incidence and course through the field will be nearer to the Sun.

Likewise in the phenomenon of bending of a light beam in the Sun's energy field also, as has been discussed in the previous section, according to this theory, the fields in the vicinity of energy intensive objects and matter intensive objects have opposite properties. The field in the vicinity of energy intensive objects has high energy intensity of space and low magnitude of space (size) whereas the field in the vicinity of high matter intensive objects must have high magnitude of space but low magnitude of intensity of energy. The nature of gravitation or repulsion between high energy intensive and matter intensive objects have also been discussed. It has been explained how, for an incident radiation passing through a field of certain space intensity, the resultant radiation is affected and its associated space intensities and space magnitudes are modified and its course is shifted towards or away from the source like the Sun creating the field. In Fig. 4(a), it was seen that an incident radiation from outside, while passing through the field due to an energy intensive object like the Sun, will pass through curve or orbital course associated with constant magnitude of space. Fig. 4(b), is similar to Fig. 4(a), in which only a ray of light radiation from outer source passing through the vicinity of the Sun has been explained. If PX is the incident radiation to the Sun's field and the position of earth is E, during a solar eclipse, the Sun will not be visible from E as indicated by the shaded cone. If the intensity of energy associated with

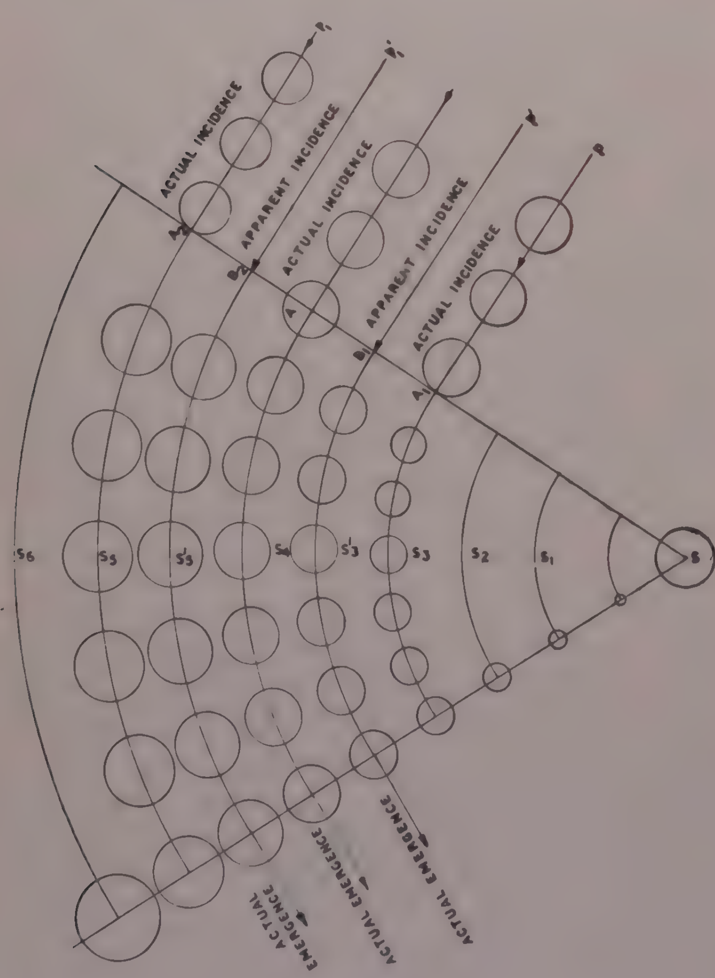

Fig. 4(a)

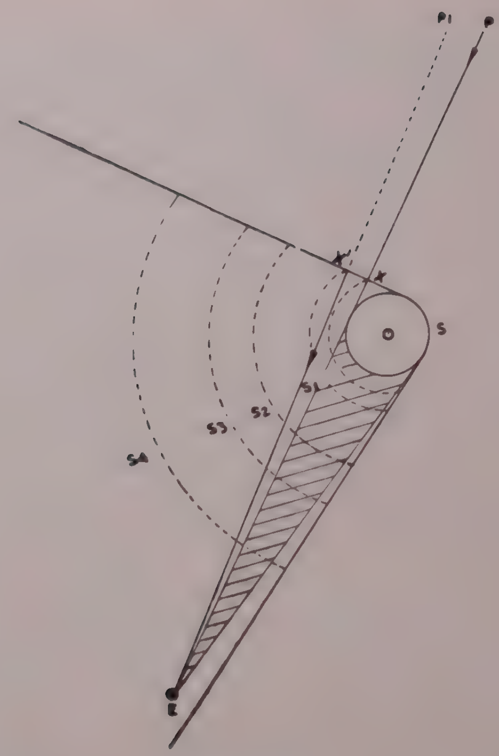

Fig. 4(b)

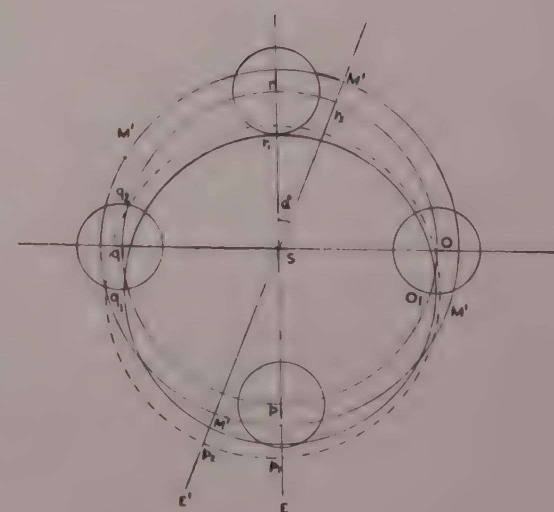

Fig. 5

incident radiation PX has to pass through the vicinity of the Sun without merging into the Sun, then the magnitude of associated space with incident ray would have to be higher than that of the space in the vicinity of the surface of the Sun. When the incident ray PX, having certain magnitude of associated space, would enter the field in the vicinity of the Sun, it would assume a resultant magnitude of space which is higher than the magnitude of space in the vicinity of the Sun and lower than that of the incident ray. Thus, the course of the resultant radiation, while passing by the Sun, will follow the curved orbital surface, say, through S_1 (not along the surface of the Sun), and would be propagated to earth along S_1E as indicated in the figure. The shift of the resultant ray has occurred from the incident point in the vicinity of the Sun to the curved surface S_1, giving the impression that $P_1X'_1$ is the incident ray instead of PX. The apparent shift of the incident ray in the direction P_1S_1 is due to two factors—one, the radial outward shift of the passing radiation due to increased resultant magnitude of associated space and the other, the course to be followed along curved equipotential surface S_1 relative to the Sun.

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*2. *Idem*, Energy Field of the Universe and Atom, Part II. The Theory of Universal Spherical Wave and Modern Science, *Technol* 2 (4) (1965), Spl. Issue.

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π-σ Theory of Anti-Particle*

By

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Dirac's interpretation to his relativistic equation for electron is criticized and an alternative interpretation based on the concept that all the laws of Physics should not be symmetrical between positive and negative electrical charges is proposed. The existence of anti-matter in general, independent of matter is ruled out and thus it is shown that the existence of anti-universe should not be a possibility.

Introduction

The expression for the probability density as obtained from Klein-Gordon equation is given by:

$$\varrho = \frac{E}{\mu c^2} \bar{\Phi} \Phi \quad .. \quad (1)$$

For E $\approx \mu c^2$ this equation reduces to the expression for the probability density in non-relativistic quantum mechanics. It is obvious from equation (1) that ϱ can have both positive values in some region of space and negative values in some other region which is physically absurd. Thus, Dirac in 1928, in order to eliminate the negative probability densities argued that expression (1) must be independent of the time derivatives meaning thereby that the required wave equation must be free from time derivatives other than first order. Therefore, the new equation as Dirac thought must be a first order linear differential equation in four dimensional space. Considering all these points Dirac arrived at the equation:

$$\left\{ p_0 + \frac{e}{c} A_0 - \rho_1 \left(\sigma, p + \frac{e}{c} A \right) - \rho_3 mc \right\} \Psi = 0 \quad .. \quad (2)$$

which he considered as the fundamental wave equation of the relativistic theory of the electron.

Putting $\alpha_1 = \rho_1\sigma_1$, $\alpha_2 = \rho_1\sigma_2$, $\alpha_3 = \rho_1\sigma_3$ and $\alpha_m = \rho_3$ equation (2) becomes:

$$\left\{ (p_0 + \frac{e}{c} A_0) - \alpha_1(p_1 + \frac{e}{c} A_1) - \alpha_2(p_2 + \frac{e}{c} A_2) - \alpha_3 (p_3 + \frac{e}{c} A_3) - \alpha_m mc \right\} \Psi = 0 \quad ..(3)$$

Then the negative energy solution of equation (3) in which the matrix element representing α_1, α_2 and α_3 are real but that of α_m is zero or non existing is given by:

$$\left\{ (-p_0 + \frac{e}{c} A_0) - \alpha_1 (-p_1 + \frac{e}{c} A_1) - \alpha_2 (-p_2 + \frac{e}{c} A_2) - \alpha_3 (-p_3 + \frac{e}{c} A_3) + \alpha_m mc \right\} \bar{\Psi} = 0 \quad .. \quad (4)$$

Now let Ψ_1 be any solution of the wave equation (3), then Ψ_1 has for its complex conjugate $\bar{\Psi}_1$ a solution of equation (4) and if Ψ_1 stands for a negative value of $cp_0 + eA_0$, then $\bar{\Psi}_1$ corresponds to the positive value of $cp_0 - eA_0$. Thus it can be seen that the operator of equation (4) is arrived at by putting $-e$ for e in the operator of equation (3) and this finally led Dirac to propose his "Theory of the Positron". Thus he was able to state that ordinarily an electron can exist in two different energy states viz. positive and negative energy states each symmetrical to certain forbidden region called the zero energy level. He further postulated that nearly all the negative levels are filled with electrons and interpreted the "hole" created as a result of ejection of an electron from one of these levels to a positive level as positron. This theory was

*Although this work was done by the author some three years ago, he came to know about Fitch experiment on the decay of K^0_2 meson (case of CP violation in weak interaction) only in July this year when Franzini etc., of Columbia reported in their experiment on the decay of eta meson the case of CP violation in electromagnetic interaction.

accepted as a correct one immediately after Anderson actually encountered positron in his cloud chamber experiment in 1930.

The impact of Dirac's concept and subsequent encountering of a number of different anti-particles in laboratories and studies of their physical behaviour later on compelled physicists to believe in the concept that all the laws of nature are identical between matter and anti-matter (the concept of Charge Conjugation Invariance). Thus emerged the idea of existence of anti-universe which is now being considered as a certainty.

Criticism

Although, Dirac's theory brilliantly predicted the existence of positron yet there are points which argue very strongly against the theory as it is evident from the following facts:

(1) The certain zero energy region E=0 in Dirac's argument is physically undefined and unexplained.

(2) His "negative levels", which have not as yet been given any proper sense, appear to be merely a result on paper.

The "filled negative levels" have been attributed "nothing" and "empty negative level" "moving positron" sense for his explanation. Taking it to be correct for the moment, the pair-production according to Dirac occurs when an electron from a "filled negative level" that is from "nothing" is raised to an "empty positive level". And this statement becomes very confusing because an electron is not "nothing" but it is something and how can something be raised out of nothing? Hence the "filled negative levels" cannot be interpreted as nothing but as something else which must be cleared.

(3) Although Dirac's negative ocean consists of almost infinite number of electrons (a case of many body problem) yet for pair production phenomena he has treated it only as a single body problem. But if many body problem is considered, there is definitely a finite probability for an ejected electron not reaching an empty positive level at all due to multiple collisions (interactions) with other electrons; thus the probability of an electron in reaching the positive energy region from negative energy region is given by:

$$P_{\uparrow} = \frac{1}{N};\ N=1, 2, 3, \ldots\ldots \quad \propto$$

Thus for more and more negative energy electron N increases and the value of $P_{\uparrow}$ would tend towards zero and finally for the greatest negative energy electron $P_{\uparrow} \approx 0$ because $N \approx \propto$ that is the probability of pair production for this electron would be zero ($P_{pair}=0$).

(4) The formation of a positron track should not be possible in Dirac's ocean because, for a "hole" in completely filled Dirac's ocean there would be no empty space available for its movement until and unless the electrons in the vicinity are completely removed and the surrounding space is made vacant for its movement for the formation of its track at the cost of extra energy.

(5) Dirac has maintained that an electron in a positive level has minimum positive energy equal to $+m_0c^2$ and that in a negative level, $-m_0c^2$. Here the logical analysis of this statement reveals that Dirac's argument necessarily attributes to the property of space which makes the electron energy positive or negative. That is, the space above E=0 has positiveness and space below it has negativeness and only then m_0c^2 (which is an absolute quantity in whichever state it may be considered) can have positive or negative sense. But this cannot be the case because space by itself should have no such properties, and even if it will have any property of its own it will be one and the same all over (that is space above and below zero state or any other space).

In fact, property of a certain region of space is the property of the matter contained by it or in its vicinity. That is why different kinds of matter such as proton, neutron etc. impart different properties to the surrounding space and exactly like masses attribute exactly same properties to the surroundings. Then, how is it so that the same electron will have positive energy in space above E=0 and negative energy below it? Hence there is *absolutely no point* in saying that ordinarily an electron can occupy both positive and negative levels in the same absolute space.

All these above considerations point out that Dirac's positron theory is inadequate and that it is based on too many arbitrary assumptions. Hence, there is a need of it being replaced by a more suitable theory.

Alternative Theory

By returning to abandoned Huygen's Ether Concept*, it is assumed that all the space in the universe is

*It is interesting to note that K. R. Chakravorty too in his theory of Universal Spherical Wave of the "Energy Field of the Universe and Atom", (Part I, Technol., 1964, 3 Spl. issue and Part II, the Theory of Universal Spherical Wave and Modern

filled up with material medium which is normally universal, continuous and all-pervading. Represented by π—state, this medium is present even in the inter-nuclear space of the innermost atoms of things like sun, stars, etc. but it is not within the space occupied by an independent particle which is the most compact tiny mass.

The π—state, which is the most normal state of universe always prefers to remain in its inertial state. An elementary particle has its existence in a $\overset{+}{\sigma}$ state which during its existance creates a "hole" in π—ocean by not allowing the π—medium to occupy the space occupied by it because it is the most compact form of matter. Thus, this "hole" stated to be in $\overset{-}{\sigma}$ state is evidently caused by corresponding $\overset{+}{\sigma}$ state. These two states always occurring simultaneously, are the abnormal states of Nature.

All the observable physical phenomena occur and physical entities exist at the background of π—state, necessarily involving both the $\overset{+}{\sigma}$ and $\overset{-}{\sigma}$ states and the physical nature of the event has always a tendency to ultimately mingle into π—state. The whole process in short may be represented as:

$$\overset{-}{\sigma} \rightarrow \pi \leftarrow \overset{+}{\sigma} \qquad .. \ (5)$$

The physical nature of π—ocean is such that its direct experimental detection is impossible. This is so because any observation in this connection would essentially envolve either $\overset{+}{\sigma}$ or $\overset{-}{\sigma}$ state of both which is different from π—ocean. Thus in four dimensional space time continuum:

$$\frac{\delta \pi}{\delta(x, y, z, t)}=0 \qquad .. \ (6)$$

corresponds to non-observable physical events. But for any observable events:

$$\frac{\delta \pi}{\delta (x, y, z, t)}=\tau \qquad .. \ (7)$$

where τ being any non-zero and real quantity.

For different independent particles there are different $\overset{+}{\sigma}$ states and thus different corresponding $\overset{-}{\sigma}$ states. For spinning particle (5) takes the form:

$$\overset{-}{\sigma} \longrightarrow \pi \longleftarrow \overset{+}{\sigma}$$

or

$$\overset{-}{\sigma} \longrightarrow \pi \longleftarrow \overset{+}{\sigma} \qquad .. \ (8)$$

For spinless particle (5) may be represented as:

$$\overset{\circ}{\overset{-}{\sigma}} \longrightarrow \pi \longleftarrow \overset{\circ}{\overset{+}{\sigma}} \qquad .. \ (9)$$

The two states $\overset{+}{\sigma}$ and $\overset{-}{\sigma}$ in normal conditions are mingled with each other. But when any $\overset{+}{\sigma}$ state due to an electron say, is given sufficient kinetic energy such that it during its flight leaves behind its image—a "hole" in π—ocean, this "hole" takes some finite but very small time to return to π—state and then anti-particle that is positron in this case, is said to have been encountered. Thus encountering of any anti-particle is nothing but separation of its $\overset{-}{\sigma}$ state from the corresponding $\overset{+}{\sigma}$ state for some finite time only and this shows that such a short life-time of an anti-particle should be their inherent property. But in the vicinity of an electron cloud or other $\overset{+}{\sigma}$ cloud a positron will be more quickly destroyed than that by π—state alone because electrons or other $\overset{+}{\sigma}$ cloud being at higher level will more quickly rush to the "hole" to bring it back to the initial π—state. Hence anti-particles should be nothing else than the holes of particles in π—ocean. From this the mechanism of positron track formation can be understood as the motion of electron in π—ocean which would mean

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Science, *ibid* 2, (1965), 4 Spl. issue) has revived the Huygen's Ether Concept by stating "The Universal Space is field of force due to energy". In his own words—"the inanimate universe in this theory consists of four dimensions, energy, matter, space and time. The energy creates space and matter occupies position in space describing time. The evolution of the universal field occurs through space assuming tetrahedral configuration leading to the manifestation of the universe as the spherical wave of energy and matter. Space in the configuration is radial and time is orbital. Highest magnitudes of intensities of energy and matter determine the centre and the boundary respectively of the spherical wave establishing their respective potential gradients in between. Space field covered within the spherical wave is full of energy as force like ether but having gradient intensity of space as force between the centre and the boundary. Energy is intensity of space and matter intensity of time. The difference between ether and space of this theory as energy field lies in that the space field is not filled with any ether-like fluid but space itself is energy". Chakravorty has also shown why "ether" could not be detected in the famous Michelson-Morley experiment. In fact Dirac's positron theory also revives Huygen's Ether concept but in a new fashion.

that all the space as Dirac has stated should not be filled (packed) with electrons.

Most of the drawbacks of Dirac's theory seem to have been eliminated in this new theory. Thus ours is the $\pi-\sigma$ universe and any thing beyond this is out of human imagination. Then after a little further consideration it can be predicted that: (1) Dirac's statement that all the laws of physics are symmetrical between positive and negative electrical charges should not be valid because an anti-particle should always lag behind its particle thereby indicating that the total energy associated with an anti-particle during its flight should always be lesser than that associated with the particle. This effect should be more pronounced in case of high energetic pair as calculated below:

Let at any instant an anti-particle lags behind its particle by an infinitely small distance Δs. Now if the coordinates of the starting and the end points of the particle in four dimensional space time continuum be (x_1, y_1, z_1, t_1) and (x_2, y_2, z_2, t_2) respectively with respect to an arbitrary fixed point of origin then clearly:

$$\Delta s = f(x, y, z, t)$$

and the total distance by which anti-particle will be behind its particle in moving from point (x_1, y_1, z_1, t_1) to point (x_2, y_2, z_2, t_2) would be: by assuming that the motion of the particle is such that even if any one of the coordinates changes, all the rest coordinates also vary automatically, although it may not necessarily be so in all cases,

$$S = \int_{x_1, y_1, z_1, t_1}^{x_2, y_2, z_2, t_2} \Delta s \qquad ..(10)$$

Here let us assume that:

$$s \rightarrow h\delta\epsilon$$
$$x_1, y_1, z_1, t_1 \rightarrow E_1$$
$$x_2, y_2, z_2, t_2 \rightarrow E_2$$

The numerical value of $\delta\epsilon$ in expression $\Delta s \rightarrow h\delta\epsilon$ gradually decreases as the particle moves towards its terminating point, h being Planck's constant and $\delta\epsilon$ an operator which operates on h thus changing its numerical value. But when this $\delta\epsilon$ occurs alone it has got the dimension of energy only. Thus in case of very high energetic quantum particles $h\delta\epsilon$ may prove to be valuable instead of h alone.

Then total energy difference between the pair will be given by:

$$\epsilon\ \text{total} = \int_{E_1}^{E_2} h\delta\epsilon$$

where ϵ total$=f(s)$

$$\text{or } \epsilon\ \text{total} = h\,(E_2 - E_1) \qquad .. (11)$$

The expression (11) can also be written as:

$$\epsilon\ \text{total} = h\,\Delta E \qquad .. (12)$$

where $\Delta E = (E_2 - E_1)$

The units of the right-hand side of expression (12) is erg sec.$\times$erg, but let us treat this to be equivalent to erg sec. only (the magnitude of $h\,\Delta E$ would remain unchanged). Then erg stands for $h\,\Delta E$ and the second for the time interval Δt which in the above case is equal to $(t_2 - t_1)$. For Planck's constant h also the same concept is applicable. In strictest sense when we say that the energy of a particle is E it must essentially be understood simultaneously that the energy of the particle is E in some time interval Δt say. This is because in no case we are ever able to measure the energy of a particle or a system just at a point but on the other hand we are able to do so which involves a range of space Δs say; $\Delta s = f(x, y, z, t)$. This Δs must be a function of Δt. An important physical conclusion may be arrived here that for any physical event both $h\,\Delta E$ and Δt are simultaneously envolved and that no physical event can occur if any one of them be thought to be absent. Thus

$$\phi(\Delta E) \rightleftharpoons \phi(\Delta t)$$

where $\rightleftharpoons$ indicates that both ΔE and Δt are supplementary to each other for the same event and its full description, such that

$$\phi(\Delta E)\phi(\Delta t) = 1$$

which shows that if in any event ΔE is more, Δt will be less and vice versa provided the event is to occur only within the same two points (these points being limiting points for the event to occur) in four dimensional space.

Thus it can be, with the help of expression (12) predicted that if an independent particle irrespective of its charge or spin be supplied an amount of energy equal to 10^{27} ergs in the form of kinetic energy at time t_1 and its complete track formed when its kinetic energy becomes zero at time t_2, be photographed it would be noticed that the complete track of the anti-particle would be smaller than that of its particle by a distance S corresponding to energy ϵtotal, indicating thereby that the total integral energy of anti-particle

will be lesser than that of particle by 6.624 ergs in time interval $\triangle t=(t_2-t_1)$.

As we have not yet been able to accelerate any elementary particle to such a tremendous energy value in our laboratory, an experiment for this purpose may be carried out with primary cosmic ray particles at the top of the atmosphere in a rocket or a satellite. (2) The existence of anti-universe should not be a possibility.

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The author's sincere thanks are due to Professor Dr. Bernard T. Feld for his encouraging advices and valuable criticisms. He would also like to thank Dr. K. R. Chakravorty, Dr. N. G. Basak of Central Fuel Research Institute, and Dr. B. K. Banerjee for encouragement.

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CONTENTS

EDITOR: S. N. ROYE

TECHNICAL ASSISTANT: BENOY K. BANERJEE

EDITOR'S NOTE

It has now been decided to publish in *TECHNOLOGY* research papers from scientists and technologists outside FCI Ltd., provided these are:

(*i*) original and related to fertilizers,

(*ii*) approved by external referees chosen by the Editor, and

(*iii*) communicated from reputed institutions, and written by workers with adequate experience.

Papers for publication in *TECHNOLOGY* are therefore welcome. These should be sent in duplicate (complete with illustrations and abstracts) to the Editor.

Selective Extraction of Potassium from Sea Water, Bitterns and Mixed Salt

By

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Sea water, bitterns etc. were treated with mexan (magnesium dipicrylaminate) for obtaining potassium dipicrylaminate, which was decomposed with nitric acid of a particular concentration to obtain potassium nitrate and dipicrylamine. The dipicrylamine could be reused for extraction of fresh amount of potash. The potassium nitrate solution containing dissolved dipicrylamine was passed through active charcoal column and evaporated to crystallize out the salt. The dipicrylamine adsorbed in active charcoal was recovered by acetone extraction. The active charcoal was reused for further adsorption of dipicrylamine.

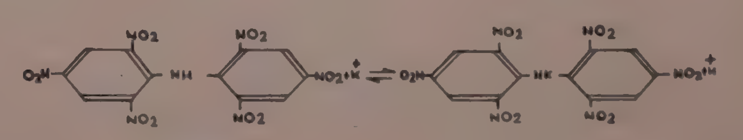
Introduction

As far back as 1933, Poluektov[1] had used ammonium salt of dipicrylamine as a spot test reagent for detection of potassium. A similar work was done by C. Cimerman[2] and C. J. Rzymowska. The extraction of potash from sea and saline water sources, however, had attracted the attention of many scientists since the preferential precipitation of potassium from its aqueous solution using dipicrylamine was developed by Kolthoff[3] and Bendix. Investigators in different countries concentrated their attention for developing a commercial process for extraction of potash. Kielland[4] patented a process based on 75 per cent recovery of potash from sea water by treating lime and dipicrylamine. Some work in this direction had also been reported from Italy[5,6] and Japan[7]. Recently Butt[8] et al reported recovery of potash from artificially prepared sea water concentrates using sodium dipicrylaminate.

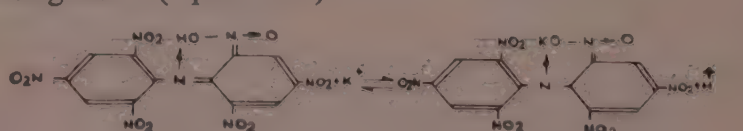
Countries like India, with little resources of mineral deposits of potash, may have to depend upon saline water sources to meet their potash requirement. A detailed study on extraction of potash by mexan from saline water sources was therefore undertaken in the laboratory.

Theoretical

Dipicrylamine, on treatment with sodium, ammonium, calcium and magnesium hydroxides, forms corresponding soluble salts. When a potassium salt is added to the solution an orange-red crystalline precipitate of potassium dipicrylaminate is formed. There are two different views on the formation of potassium dipicrylaminate. One view is that the formation of the complex is due to the replacement of hydrogen atom in the amine group. (equation 1).



The other view which seems to be more correct is that formation of KDPA is due to replacement of the hydrogen atom of the hydroxyl group in the enol form to give a compound having the following structural arrangement (equation 2).



The extraction of potash by magnesium dipicrylaminate is given by the following equations.

$$(Mg^{2+})\ DPA + K^+ \rightleftharpoons KDPA + Mg^{2+}$$

The chelating agent could be regenerated with strong acids.

$$KDPA\ (S) + HNO_3 \rightleftharpoons HDPA\ (S) + KNO_3$$

In the gravimetric estimation of potash- the mexan nsed was 50 per cent in excess of the stoichiometric value for the complete precipitation of potassium as KDPA. It was possible to determine 0.2—0.4 mg. of potash within an approximation of 0.5—1.0 per cent of the true value, even in the presence of as much as 8 mg. of sodium. Any chelate of dipicrylamine, like sodium dipicrylaminate and calcium dipicrylaminate, may be used for the extraction of potash.

In this study mexan was prepared for two reasons. Generally sodium dipicrylaminate solution as prepared with dipicrylamine and sodium carbonate in stoichiometric ratio has a pH in between 8.7 and 8.9. Preliminary investigations had shown that with bitterns of above pH 8, some precipitate of magnesium hydroxide is formed. On the other hand, calcium dipicrylaminate if used may give rise to calcium sulphate as a precipitate by interaction of calcium-chloride formed with sulphate ions present in bitterns and mixed salt solutions.

As will be evident from the above equation, stoichiometric quantity of mexan (by weight) required is eleven times that of potassium present and use of dipicrylamine in excess will be economically prohibitive in case of industrial processes. It would be therefore better to carry out the reactions using an excess of potash to consume all the reagent, if possible. Potash recovery in such cases may not be complete but may be confined to the economic limits. Unreacted mexan going out with the outflow bittern may be decomposed by acid treatment and the dipicrylamine recovered for reuse.

Experimental

Preparation of Mexan: For the gravimetric estimation of potassium it is generally recommended that in order to prepare mexan of suitable concentration magnesium oxide and HDPA should be taken in the ratio 0.416 : 1 (by wt.) in a given quantity of water. Stoichiometrically however, a ratio viz. 0.0456 : 1 (by wt.) should have sufficed. Experiments were carried out in order to determine the optimum concentration of mexan obtainable by treating a fixed quantity of HDPA (prepared in the laboratory with minimum excess of technical grade* magnesium oxide required stoichiometrically. Experimental results are shown in Fig. 1.

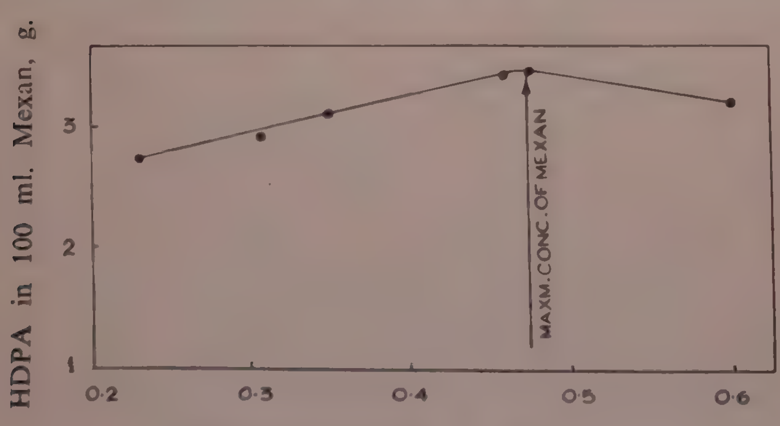


Fig. 1—Concentration Curve of Mexan at 30°C (Reaction time: 8 hours).

It was observed that when HDPA and magnesium oxide were taken in the stoichiometric ratio in 200 ml. of distilled water and the mixture stirred continuously for 8 hours, a solution of mexan containing 1.675 g. HDPA per 100 ml. was obtained. When the quantity of magnesium oxide was raised to twice the stoichiometric value mexan concentration was found to be 2.395 grams HDPA per 100 ml of reagent. However, the highest concentration of mexan was obtained, when magnesium oxide taken was slightly more than twice the stoichiometric quantity required (Fig. 1) i.e. 2.436 g. HDPA per 100 ml. of mexan. The reaction was almost quantitative and further addition of magnesium oxide did not increase the concentration of mexan. The mexan of the maximum concentration thus obtained was used in all the following experiments.

Treatment of Sea water, Bitterns and Mixed Salt Solution with Mexan: Experiments were carried out by treating equal quantities of mexan of same concentration with varying volumes of sea water, bitterns of different composition (vide Table 1) and mixed salt solution containing more or less equal quantities of potash. For this purpose sea water and bitterns[9] as are normally found in Indian salt works viz Tata Chemicals Mithapur, Wadala salt works Bombay, Kharaghoda and Bhavnagar salt works were artificially prepared in the laboratory by dissolving requisite quantities of different salts and finally determining the concentration of individual constituents (sodium chloride by difference).

The reaction was carried out at room temperature (28-30°C) and reaction time given was 30 min. The reaction mixture was filtered through a G/4 sintered glass crucible. The precipitate of KDPA was washed with saturated solution of KDPA and finally with a little ice cold water and dried at 110°C. The effect of settling time i.e. 8, 12 and 24 hours on the yield of KDPA was not distinguishable. Similarly, experiments were conducted by varying the volume of potassium source added in order to study the effect of excess potash in the

*Obtained from International Mercantile Ltd., Calcutta

TABLE 1—COMPOSITION OF SEA WATER, BITTERNS AND MIXED SALT

	Sea Water	Bittern A	Bittern B	Bittern C	Bittern D	Bittern E	Bittern F	Mixed Salt
Density, °C Be	3.5	29.00	30.00	30.00	34.50	34.50	29.00	—
Sp. gr.	1.025	1.25	1.27	1.27	1.32	1.32	—	—
Temp., °C	—	—	34.00	—	34.00	34.00	—	—
NaCl, %	2.85	9.20	10.50	7.50	1.60	1.60	10.20	22.00
$CaSO_4$, %	Traces	0.30	0.30	—	—	—	—	—
$MgSO_4$, %	0.22	5.60	5.90	6.70	7.01	10.10	8.35	33.00
$MgCl_2$, %	0.36	12.00	10.10	15.00	22.10	17.90	15.08	3.00
KCl, %	0.08	2.10	2.10	4.90	2.30	2.40	2.49	18.00
Br, %	Traces	0.18	0.18	—	0.30	—	—	—
Water, %	96.49	70.62	70.62	65.90	66.70	68.00	—	24.00

Note: Bitterns A and D — Tata Chemicals, Mithapur, Okhamandal, Gujarat
Bitterns B and E — Wadala Salt Works, Bombay.
Bittern C — Kharaghoda Salt Works, Kharaghoda, Gujarat.
Bittern F — Bhavnagar Salt Works, Bhavnagar, Gujarat.

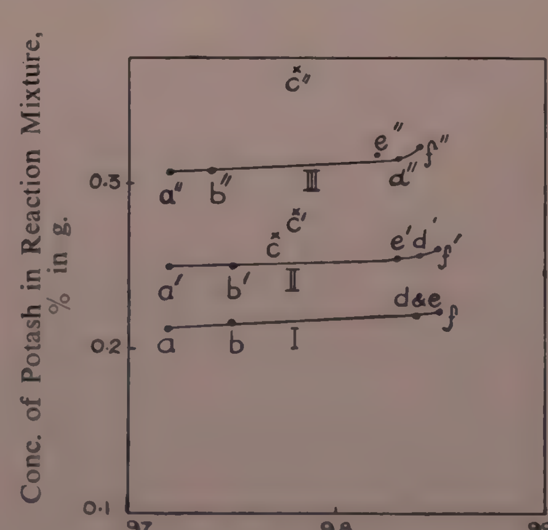
system on recovery of KDPA (Table 2). When sea water and bitterns were treated with mexan in stoichiometric ratio the corresponding recovery of KDPA was 69.1 and 93.2 - 94.2 per cent respectively. It was noticed that with 25-30 per cent excess potash about 4 per cent more KDPA could be precipitated, in case of bitterns and mixed salt further addition of potash had little effect on the recovery of KDPA.

Results and Discussion

Table 2 shows that in case of sea water, when reaction was carried out in stoichiometric ratio of the reactants, recovery of KDPA was only 69.1 per cent. By increasing the quantity of potash in the system by further addition of 100 ml. sea water, recovery of HDPA was 79.1 per cent as KDPA. Further addition did not increase the yield of KDPA and unused mexan in the outflow got more diluted. The total recovery of HDPA after acid treatment of unused mexan in the outflowing sea water was 98.53 per cent and 1.47 per cent of the HDPA used in the reaction remained in solution (500-600 ml.). The recovery of this amount of dipicrylamine from so large a volume of dilute solution would pose a problem for industrial scale operation. In case of bitterns, when the reaction was carried out in the stoichiometric ratio of the reactants, the quantity of KDPA obtained was 93.2 - 94.2 per cent of the theoretical amount. It was also observed that percentage recovery of potash varied from bittern to bittern and was not in accordance with potash concentration in the bitterns.

With increase in potash content in the system by 25-30 per cent over the amount required stoichiometrically with more bittern or mixed salt solution, a maximum recovery of KDPA would be brought in the range 97.2-98.5 per cent of the quantity of mexan used. This, however, reduced the per cent recovery of potash from the system correspondingly.

It was rather surprising that in the case of Kharaghoda bittern, which has higher concentration of potash the recovery of potash was a little less (when treated with a stoichismetric quantity of mexan) compared to other bitterns. The recovery of potash from other bitterns (irrespective of their composition) by mexan treatment



Conversion of Mexan to KDPA, %

Fig. 2—Effect of Excess Potash on Conversion of Mexan to KDPA at 30°C.

I—With 25% excess potash
II—With 50% excess potash
III—With 100% excess potash

a, *b*, *c*, *d*, *e* and *f* represent corresponding bitterns.

TABLE 2—RECOVERY OF POTASSIUM AS KDPA BY MEXAN
(Temperature 30°C)

Source of Potassium	Volume Taken, ml.	Potassium, g.	Mexan Added, ml.	HDPA/ml. of Mexan, g.	KDPA Collected, g.	KDPA Calculated, g.	HDPA Recovered as KDPA, %	Potassium Reacted with Mexan, %
Sea Water	*500	0.2094	98	0.0242	1.7695	2.5609	69.1	69.1
	600	0.2513	98	0.0242	2.0256	2.5609	79.1	66.0
	700	0.2932	98	0.0242	2.0000	2.5609	78.1	55.8
Bittern 'A'	*20	0.2190	102	0.0243	2.5229	2.6783	94.2	94.2
	25	0.2738	102	0.0243	2.6033	2.6783	97.2	77.8
	30	0.3285	102	0.0243	2.6030	2.6783	97.2	64.9
	40	0.4380	102	0.0243	2.6031	2.6783	97.2	48.6
Bittern 'B'	*20	0.2190	102	0.0243	2.5202	2.6783	94.1	94.1
	25	0.2738	102	0.0243	2.6113	2.6783	97.5	78.0
	30	0.3285	102	0.0243	2.6110	2.6783	97.5	65.0
	40	0.4380	102	0.0243	2.6086	2.6783	97.4	48.7
Bittern 'C'	*10.0	0.2560	119	0.0242	2.9176	3.1308	93.2	93.3
	12.5	0.3200	119	0.0242	3.0587	3.1308	97.7	78.2
	15.0	0.3840	119	0.0242	3.0609	3.1308	97.8	65.2
	20.0	0.5120	119	0.0242	3.0607	3.1308	97.8	48.9
Bittern 'D'	*20	0.2400	111	0.0244	2.7532	2.9352	93.8	93.8
	25	0.3000	111	0.0244	2.8882	2.9352	98.4	78.8
	30	0.3600	111	0.0244	2.8880	2.9352	98.4	65.7
	40	0.4800	111	0.0244	2.8853	2.9352	98.3	49.2
Bittern 'E'	*20	0.2508	117	0.0243	2.8862	3.0672	94.1	94.2
	25	0.3135	117	0.0243	3.0181	3.0672	98.4	78.5
	30	0.3762	117	0.0243	3.0150	3.0672	98.3	65.6
	40	0.5016	117	0.0243	3.0119	3.0672	98.2	49.1
Bittern 'F'	*20	0.2560	118	0.0243	2.9460	3.1308	94.1	94.2
	25	0.3200	118	0.0243	3.0838	3.1308	98.5	75.7
	30	0.3840	118	0.0243	3.0835	3.1308	98.5	63.1
	40	0.5120	118	0.0243	3.0807	3.1308	98.4	47.3
Mixed Salt 150 g./l.	*20	0.2825	130	0.0244	3.2510	3.4549	94.1	94.2
	25	0.3532	130	0.0244	3.3927	3.4549	98.2	78.6
	30	0.4238	130	0.0244	3.3928	3.4549	98.2	65.5
	40	0.5650	130	0.0244	3.3996	3.4549	98.4	49.2

N.B.: Figures marked with * are in stoichiometric ratio with Mexan added.

was found approaching a limit and tended to follow the concentration of potash in the system and the bitterns as well when potash content was raised 100 per cent over the amount stocihiometrically required. This trend can be seen in Fig. 2, which indicates the recovery of KDPA from bitterns with varying potash concentration by increasing the quantity of potash in the reaction system.

Recovery of Potassium Nitrate From KDPA: Potassium dipicrylaminate obtained was treated with different quantities of nitric acid of various concentrations. It was found that for complete decomposition of KDPA, the minimum strength of nitric acid should be 7 N, and the amount should be three times the stoichiometric quantity. The decomposition was studied at temperature 40-60°C and the time required noted (Table 3). By

TABLE 3—TREATMENT OF KDPA WITH NITRIC ACID

Sl. No.	Pot. Dipicrylaminate Taken, g.	Normality of Acid, N	Time of Reaction, hr.	Temp., °C	HDPA		Pot. Nitrate		% Recovery of HDPA	% Recovery of KNO_3
					Calculated, g.	Collected, g.	Calculated, g.	Collected, g.		
1.	0.9879	7	6	40	0.9091	0.9073	0.2091	0.2084	99.8	99.0
2.	1.0079	7	6	40	0.9285	0.9263	0.2123	0.2102	99.8	99.0
3.	1.0064	7	5	50	0.9261	0.9247	0.2130	0.2122	99.8	98.9
4.	1.0000	7	5	50	0.9203	0.9175	0.2117	0.2090	99.7	98.7
5.	1.0035	7	4	60	0.9235	0.9212	0.2124	0.2099	99.7	98.8
6.	1.0021	7	4	60	0.9222	0.9200	0.2121	0.2090	99.7	98.5

TABLE 4—RECOVERY OF HDPA FOR RECYCLING

(Temp. 30°C)

Source of Potassium	Volume Taken, ml.	Mexan Added, ml.	HDPA Added as Mexan, g.	KDPA Recovered, %	HDPA Recovered, as KDPA, g.	HDPA from Unreacted Mexan g.	HDPA gone to solution, g.	Total HDPA Recovered, g.	HDPA in Outflow, %
Sea water	500	98	2.3716	69.1	1.6388	0.6978	0.035	2.3366	1.47
Bittern 'A'	20	102	2.4786	94.2	2.3508	0.1198	0.008	2.4706	0.32
Bittern 'B'	20	102	2.4786	94.1	2.3484	0.1222	0.008	2.4706	0.32
Bittern 'C'	10	119	2.8798	93.2	2.6739	0.1979	0.009	2.8718	0.31
Bittern 'D'	20	111	2.7084	93.8	2.5405	0.1589	0.009	2.6994	0.33
Bittern 'E'	20	117	2.8431	94.1	2.6753	0.1578	0.010	2.8331	0.35
Bittern 'F'	20	118	2.8674	94.1	2.6982	0.1602	0.009	2.8584	0.31
Mixed Salt 150 g./l.	20	130	3.1720	94.1	2.9848	0.1762	0.011	3.1610	0.34

raising the temperature, the time of decomposition could be hastened. The decomposition is completed in 6 and 4 hours at 40 and 60°C respectively. The decomposed product was treated with minimum quantity of water (8 ml./g.) to take out all potassium nitrate. The leached solution was contaminated with the dissolved HDPA, which was removed by adsorption in active charcoal. The potash in the solution coming out was determined by the standard method of sodium-cobaltinitrite. The potassium estimated was found to be 99.3 per cent of the theoretical value in KDPA (assuming latter to be 100 per cent pure). The results were further confirmed by evaporating the solution to dryness.

Recovery of HDPA for Recycling: The recovery of HDPA from unused mexan going out with the bittern and from potassium dipicrylamine by acid treatment is limited by the solubility of dipicrylamine. Experiments were carried out to determine the pH at which solubility

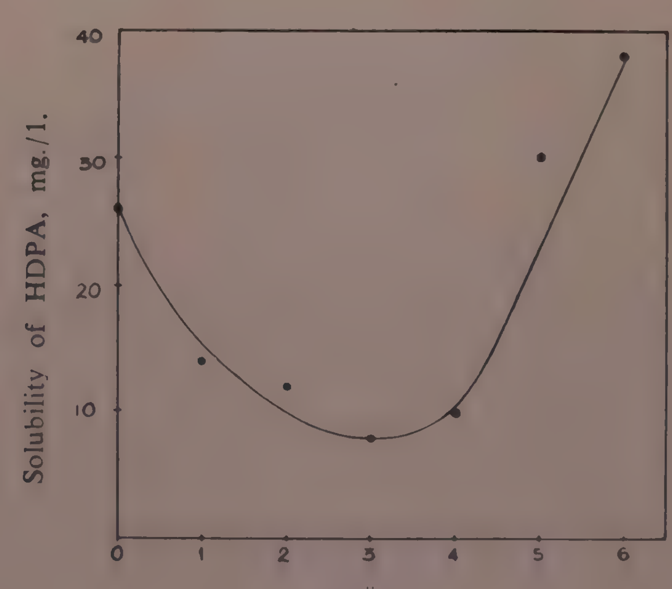


Fig. 3—Effect of pH variation of Solubility on HDPA at 28°C.

TABLE 5—RECOVERY OF HDPA FROM SOLUTION BY ADSORPTION IN ACTIVE CHARCOAL AND ACETONE EXTRACTION

(Temperature 28-30°C)

Solution Containing Dissolved HDPA		Dry Active Charcoal taken, g.	Depth of the Adsorption Column, cm.	Solution Taken, ml.	HDPA in the Solution, g/l.	HDPA Adsorbed in Active Charcoal, g.	HDPA Recovered by Acetone, g.	Acetone Used for Extraction of HDPA,, ml.
Bittern 'A'	(*i*)	4	10	1150	0.065	0.0747	0.0512	250
	(*ii*)	4	10	790	0.065	0.0513	0.0500	280
Bittern 'B'	(*i*)	4	10	1150	0.065	0.0747	0.0510	248
	(*ii*)	4	10	785	0.065	0.0510	0.0500	285
Bittern 'C'	(*i*)	4	10	1080	0.069	0.0745	0.0502	245
	(*ii*)	4	10	725	0.069	0.0500	0.0490	290
Bittern 'D'	(*i*)	4	10	1090	0.068	0.0741	0.0500	250
	(*ii*)	4	10	740	0.068	0.0554	0.0544	285
Bittern 'E'	(*i*)	4	10	1000	0.075	0.0750	0.0518	245
	(*ii*)	4	10	675	0.075	0.0506	0.0490	285
Bittern 'F'	(*i*)	4	10	1150	0.065	0.0747	0.0520	250
	(*ii*)	4	10	810	0.065	0.0526	0.0514	280
Mixed salt Solution 150 g./l.		4	10	1030	0.073	0.0751	0.0516	255
		4	10	700	0.073	0.0511	0.0500	290

N.B. (*i*) fresh active charcoal, (*ii*) once used active charcoal

of HDPA was minimum so that the recovery could be made maximum. Generally the solubility of HDPA in water is about 7-8 mg./l. at 30°C in the 2 to 4 pH range (Fig. 3). It was however found that the amount of unrecovered HDPA even at that pH (about 4) was 1.47 per cent in case of sea water and 0.3 - 0.35 per cent in case of bitterns and mixed salt solution (Table 4). Even this little amount remaining in solution would mean a loss of about 0'015-0.017 kg. of HDPA for one kg of potassium nitrate produced. As this loss will greatly affect the economics of the process of recovery of potassium on commercial scale, because of the high cost of dipicrylamine compared to potash, experiments were conducted to evolve a feasible process for complete recovery of dipicrylamine.

It was found that the active charcoal of the size 0.05 mm (E. Merck quality) effectively adsorbed the dipicrylamine from bitterns solution, and by trial it was established that the adsorbed dipicrylamine could be recovered by acetone extraction (Table 5). The same active charcoal after extraction of dipicrylamine by acetone can be reused. It was observed that some amount of HDPA adsorbed during the first adsorption was permanently held up in the active carbon used. There was a decrease in the amount of dipicrylamine adsorbed in subsequent treatment with the same active charcoal but whatever was adsorbed came out almost quantitatively by acetone extraction.

Conclusion

The limitation of the process of recovery of potash fromsaline water sources particularly bitterns by treatment with soluble salts of dipicrylamine (magnesium dipicrylaminate in this particular case) because of the solubility of dipicrylamine in the outgoing bittern and potassium nitrate solution can be overcome by passing them through a column of active charcoal and getting back the adsorbed dipicrylamine by acetone treatment. Thus from the chemical point of view the process is feasible. Viability of an industrial process will, however, depend on the (*i*) production of dipicrylamine on a large scale at low cost, (*ii*) availability of fresh water at

sea coast and (*iii*) active charcoal and acetone at a cheap price.

Acknowledgement

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Estimation of Phosphate, Sulphate and Fluosilicate in Wet Process Phosphoric Acid by High Frequency Titrimetry

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A method based upon high frequency titrimetry has been evolved for quick estimation of sulphate, phosphate and fluosilicate in wet process phosphoric acid using thin-walled polythene cells in place of the conventional glass cells. The phosphoric acid sample is first titrated against standard caustic soda; the first break in the titration curve corresponds to the complete neutralization of sulphuric and hydrofluosilicic acids and the second break to one-third neutralization of phosphoric acid. The sulphate is estimated separately by titration against the standard barium chloride.

In the manufacture of phosphoric acid by the interaction of rock phosphate and sulphuric acid, correct reaction conditions have to be strictly maintained in order to ensure the formation of an easily filterable gypsum and to attain the maximum recovery of P_2O_5 from the rock. For this purpose, samples of reaction slurry and filtered liquors are drawn out at frequent intervals and analysed for their sulphate, phosphate and fluorine contents. The standard gravimetric and volumetric methods for estimation of these ingredients are time-consuming, and hence for plant control some approximate methods are employed so that results can be obtained within a short time. For example, P_2O_5 in the filtrates is estimated by noting the specific gravity of the liquor and sulphate by measuring the volume of the precipitate formed by the addition of barium chloride[1]. Obviously, such methods have their limitations and at times may give misleading results.

It was, therefore, desirable to evolve some quick but reasonably accurate methods for the estimation of phosphate, sulphate and fluorine in liquors from the phosphoric acid plant. In this context, the application of high frequency titrimetry[2] seemed promising. This technique has been applied by Zarinskii[3–8] et al in the

estimation of several acids and bases in aqueous and non-aqueous media. Bezrogova[9] has determined hydrofluoric, hydrofluosilicic acid and sulphuric acid in their mixtures by high frequency titrimetry. A method has also been evolved in this laboratory[10] for the estimation of chloride in evaporator liquor in an ammonium sulphate plant by high frequency titrimetry.

The present investigation was undertaken to develop methods for quick estimation of sulphate, phosphate, hydrofluosilicic acid and hydrofluoric acid in liquors from phosphoric acid plant by high frequency titrimetry. Experiments have been carried out with these ingredients singly as also in various combinations. High frequency titrations have also been carried out with samples of liquors drawn from the phosphoric acid pilot plant set up in this laboratory.

Experimental

Apparatus: The high frequency apparatus used in these experiments is the same as that described earlier[11]: a frequency of 8 Mc/s is produced by a piezo-electric quartz crystal. It has a circuit which gives a direct indication of both effective overall conductance and effective overall capacitance changes in the titration cell. The titration cell in the present study was a wide-mouth polythene bottle graduated up to 400 ml. and having a wall thickness of 1 mm. and diameter 7.4 cm. Two electrodes made of copper ribbons each 1.5 cm. in breadth were wound round the cell and kept 3-4 cm. apart. So far glass cells have been used in high frequency titrimetry. The polythene cell was used successfully for the first time during these studies in order to prevent possible interaction between glass and fluoride in the liquors. The titrimeter is connected to a voltage stabililizer and the solution is stirred magnetically by means of a magnetic stirrer coated with polythene cover, except when a reading is taken. The titrant is added from a micro burettee in 0.1-0.5 ml. portions. All the chemicals used in these investigations were of A. R. B. D. H. grades and the solutions were made in doubly distilled conductivity water.

Procedure: The method used in these titrations is characterized by the fact that after every addition of titrant there is an alteration in the composition of titrating system which produces a change in frequency as a result of which the oscillation of the quartz crystal becomes slow and a change in capacity is necessary to restore full vibration in the crystal. As the composition of the solution is changed permanently, there will be a corresponding change in the resistance and dielectric constant of the solution. Hence changes in the capacity dial or meter readings can be plotted against the volume of titrant added and equivalence point noted from the break in the titration curve. Since wet process phosphoric acid contains phosphoric, sulphuric and hydrofluosilicic acids and possibly hydrofluoric acid, these ingredients were titrated separately as also in various combinations against 0.1 N caustic soda by the high frequency method. The following systems were titrated: (*a*) Sulphuric acid alone; (*b*) phosphoric acid alone; (*c*) hydrofluoric acid alone; (*d*) mixture of sulphuric and phosphoric acids; (*e*) mixture of sulphuric and hydrofluoric acids; (*f*) mixture of phosphoric and hydrofluoric acids; (*g*) mixture of sulphuric acid, phosphoric acid and hydrofluoric acids; and (*h*) wet process phosphoric acid from a pilot plant in this laboratory.

In the present study, high frequency titration of a mixture of sulphuric, hydrofluoric and hydrofluosilicic acid was not carried out since this has already been done by Bezrogova[9] et al.

In all the titrations mentioned above, the optimum concentrations of the acids or mixtures that should initially be taken in the titration cell for the maximum sensitivity of high frequency titrimeter were first found out. Stock solutions were prepared by diluting to known volumes the various acids and mixtures to be titrated and 1, 1.5 and 2 ml, etc., of these were taken in the titration cell and doubly distilled water was added so that the final level of the solutions was slightly higher than the upper edge of the upper electrode.

Results and Discussion

The results of high frequency titration of phosphoric acid against 0.1 N caustic soda (Fig. 1) show that a single break occurs in the titration curve and this corresponds to the neutralisation of orthophosphoric acid to monosodium phosphate as in the case of low frequency conductometric titration. The results of estimation (Table 1) show that the error does not exceed 3 per cent.

Single breaks are also obtained in the titration curves when sulphuric or hydrofluoric acid is estimated by the high frequency method (Fig. 1) but these breaks correspond to the complete neutralization of the acids. The errors in estimation (Table 2) in these cases are well within 2 per cent. In Fig. 2 are shown the titration curves of mixtures of (1) sulphuric and phosphoric (2) phosphoric and hydrofluoric and (3) sulphuric and hydrofluoric acids. In (1), the first break corresponds to the complete neutralization of sulphuric acid and the second break to one-third neutralization of phosphoric acid.

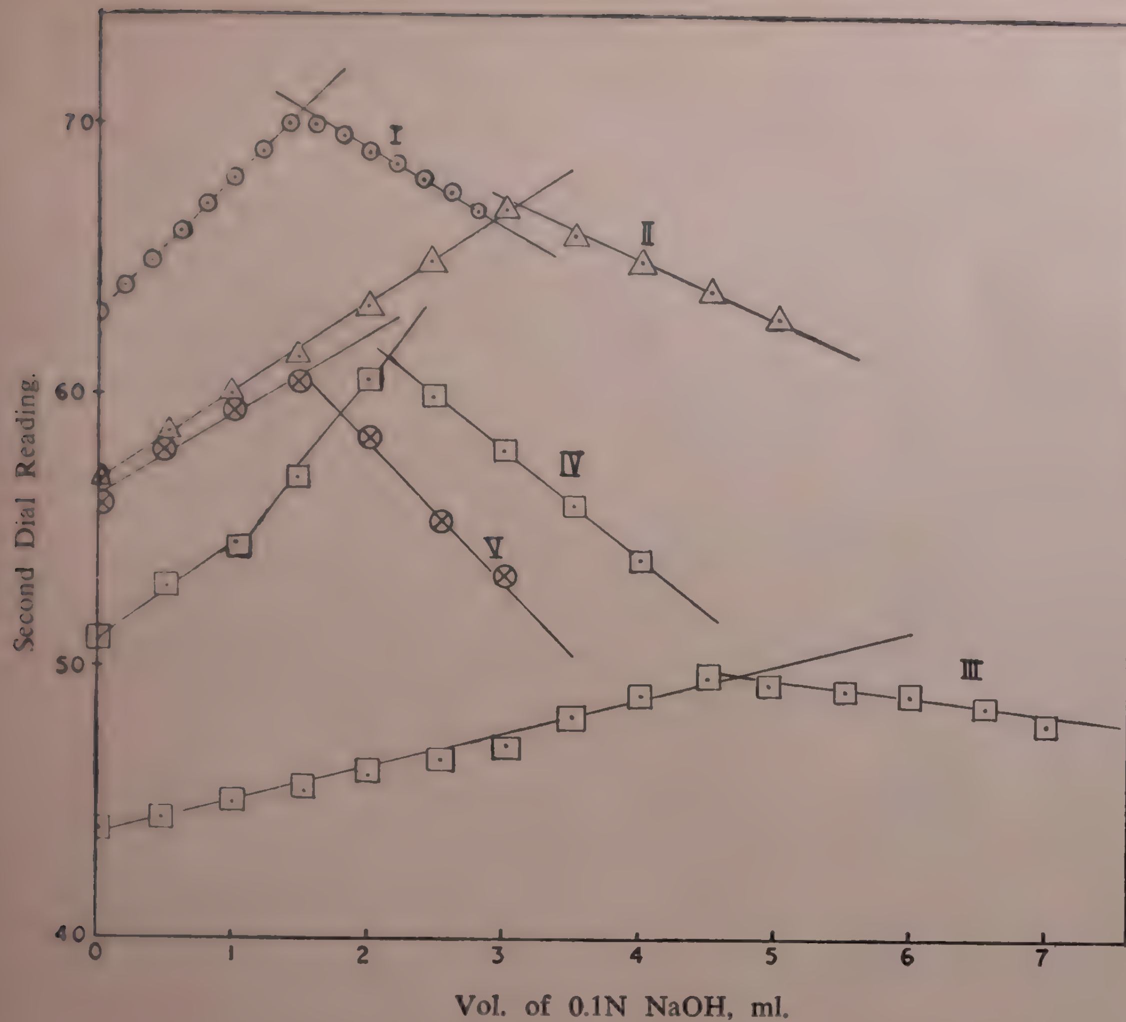

Fig. 1—High Frequency Titrations of Acids Taken Singly.
I—1 ml. H_3PO_4 Stock Soln. against 0.1N NaOH
II—2 ml. H_3PO_4 Stock Soln. against 0.1N NaOH
III—3 ml. H_3PO_4 Stock Soln. against 0.1N NaOH
IV—1 ml. H_2SO_4 Stock Soln. against 0.1N NaOH
V—1 ml. HF Stock Soln. against 0.1N NaOH

TABLE 1—HIGH FREQUENCY TITRATION OF PHOSPHORIC ACID AGAINST STANDARD CAUSTIC SODA

Nos.	Volume of Diluted Acid Taken for Titration, ml.	P_2O_5 by Gravimetric Estimation, mg.	P_2O_5 by High Frequency Titration, mg.	Error, %
1	1	10.85	10.90	0.46
2	1	10.85	10.80	0.46
3	1.5	16.27	16.20	0.43
4	1.5	16.27	16.32	0.37
5	2	21.70	21.33	1.60
6	2	21.70	22.00	1.35
7	3	32.55	33.20	1.99
8	3	32.55	33.40	2.60
9	3.5	38.00	37.00	2.63
10	4.0	43.30	42.00	3.00

TABLE 2—HIGH FREQUENCY TITRATION OF SULPHURIC AND HYDROFLUORIC ACIDS TAKEN SEPARATELY AGAINST STANDARD CAUSTIC SODA

Nos.	H_2SO_4 as SO_3, mg.			HF as F, mg.		
	Taken	Found	Error, %	Taken	Found	Error, %
1	4.40	4.38	0.45	1.55	1.53	1.28
2	8.80	8.83	0.34	3.10	3.06	1.30
3	8.80	8.76	0.45	3.10	3.13	0.97
4	17.60	17.45	0.85	6.20	6.12	1.29
5	22.00	22.30	1.36	9.30	9.42	1.27

In (2), the first break corresponds to one-third neutralization of phosphoric acid and the second to complete neutralization of hydrofluoric acid. In (3), the first break corresponds to complete neutralization of sulphuric acid and the second break to complete neutralization of hydrofluoric acid. In all these estimations, the error does not exceed four per cent (Table 3).

When a mixture of sulphuric, phosphoric and hydrofluoric acids is titrated against caustic soda by the high frequency method, the first break in the titration curve I (Fig. 3) corresponds to complete neutralization of sulphuric acid, the second to one-third neutralization of phosphoric acid and the third break to complete neutralization of hydrofluoric acid. The error in estimation is within 5 per cent (Table 4) in the concentration

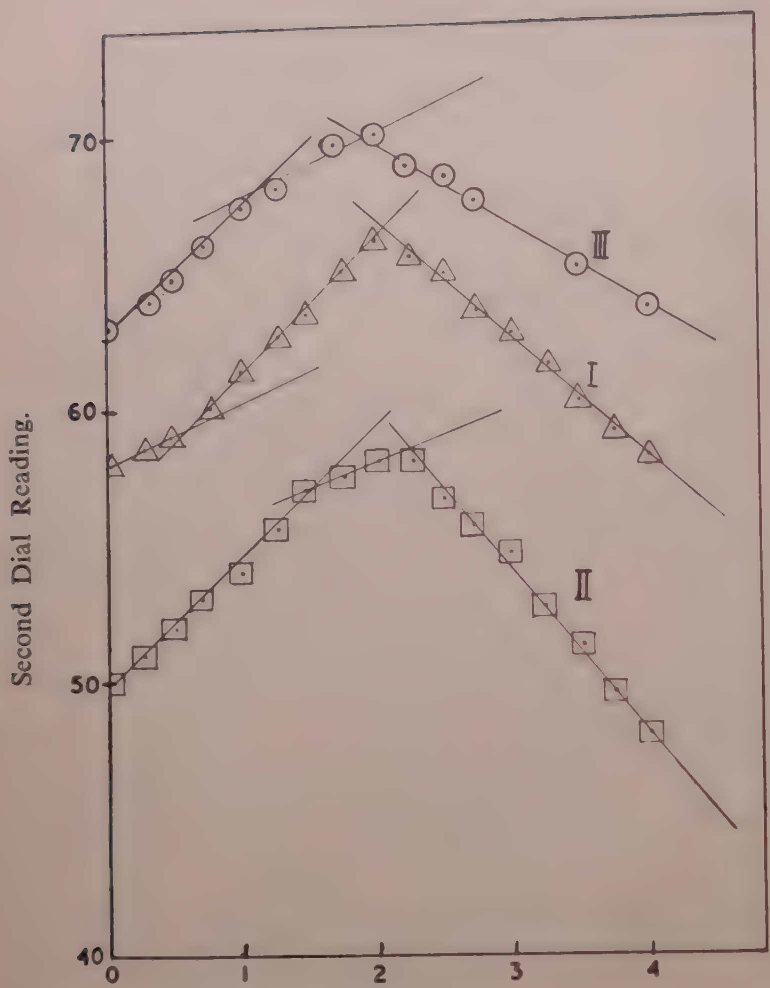

Fig. 2—High Frequency Titrations of Mixtures of Acids Taken Two at a Time.

I—0.25 ml. H_2SO_4+1 ml. H_3PO_4 against 0.1N NaOH

II—1 ml. H_3PO_4+0.5 ml. HF against 0.1N NaOH

III—0.5 ml. H_2SO_4+0.5 ml. HF against 0.1N NaOH

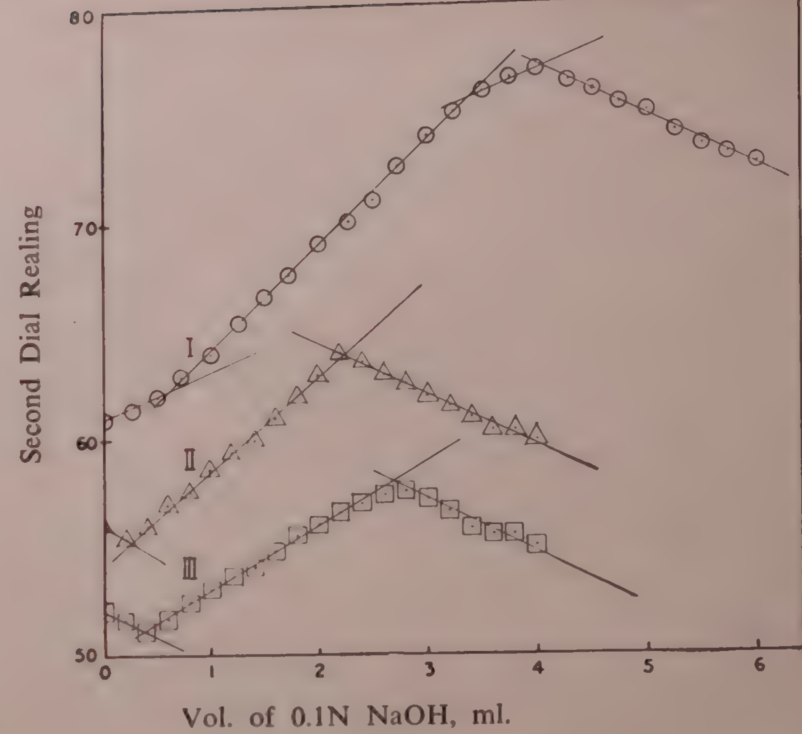

Fig. 3—High Frequency Titration of Mixed Acids.

I—0.25 ml. H_2SO_4+2 ml. H_3PO_4+0.5 ml. HF against 0.1N NaOH

II—1 ml. of Diluted Technical Phosphoric Acid (sample A) against 0.1N NaOH

III—1 ml. of Diluted Technical Phosphoric Acid (sample B) against 0.1N NaOH

ranges studied. Sharp breaks are obtained in all the titration curves corresponding to mixtures of acids mentioned above; it is not possible to get such breaks by applying low frequency conductometric method in these cases.

The titration curves II & III (Fig.3) corresponding to wet process phosphoric acid samples taken from the pilot plant show only two breaks. The first break corresponds to the complete neutralization of sulphuric acid and also of hydrofluosilicic acid: and the second break to one-third neutralization of phosphoric acid. The absence of third break indicates that hydrofluoric acid is not present in phosphoric acid samples from the pilot plant. The total fluorine present in these samples is, therefore, practically entirely in the form of hydrofluosilicic acid. The total sulphate in the pilot plant phosphoric acid has been estimated both by the standard gravimetric method and by the high frequency titration against

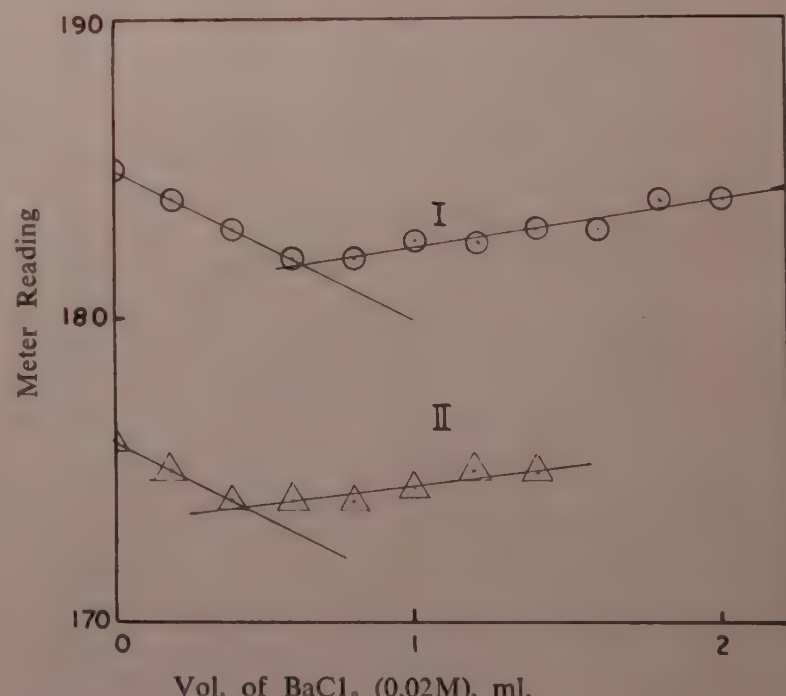

Fig. 4—Estimation of Sulphate in Technical Phosphoric Acid by High Frequency Titration.

I—1 ml. of Diluted Technical Phosphoric Acid (sample A) against 0.02M $BaCl_2$

II—1 ml. of diluted technical phosphoric acid (sample B) against 0.02M $BaCl_2$.

barium chloride (Fig. 4); there is a close agreement between the two sets of values (Table 5). The total sulphate in the strongly acidic medium may be assumed

TABLE 3—HIGH FREQUENCY TITRATION OF MIXTURES OF PHOSPHORIC, SULPHURIC AND HYDROFLUORIC ACIDS, TAKEN TWO AT A TIME

Nos.	Mixture $H_3PO_4+H_2SO_4$						Mixture H_2SO_4+HF						Mixture H_3PO_4+HF					
	Taken, mg.		Found, mg.		Error, %		Taken, mg.		Found, mg.		Error, %		Taken, mg.		Found, mg.		Error, %	
	H_3PO_4 as P_2O_5	H_2SO_4 as SO_3	H_3PO_4 as P_2O_5	H_2SO_3 as SO_3	H_3PO_4	H_2SO_4	H_2SO_4 as SO_3	HF as F	H_2SO_4 as SO_3	HF as F	H_2SO_4	HF	H_3PO_4 as P_2O_5	HF as F	H_3PO_4 as P_2O_5	HF as F	H_3PO_4	HF
1	10.85	2.20	10.80	2.18	0.46	0.91	4.40	1.55	4.42	1.52	0.45	1.93	10.85	1.55	10.95	1.58	0.92	1.93
2	10.85	4.40	10.89	4.35	0.40	1.13	4.40	3.10	4.45	3.02	1.13	2.40	10.85	3.10	10.70	3.00	1.37	3.20
3	21.70	4.40	21.53	4.45	0.70	1.13	8.80	1.55	8.72	1.49	0.91	3.80	21.70	1.55	21.50	1.51	0.92	2.50
4	21.70	8.80	21.90	8.70	0.92	1.14	8.80	3.10	8.70	3.14	1.13	1.28	32.55	3.10	32.20	3.18	1.08	2.45
5	32.55	8.80	32.02	8.95	1.60	1.70	17.60	3.10	17.40	3.00	1.13	3.20	43.30	3.10	42.00	3.00	3.00	3.20

TABLE 4—HIGH FREQUENCY TITRATION OF PREPARED MIXTURE OF PHOSPHORIC, SULPHURIC AND HYDROFLUORIC ACIDS

Nos.	H_2SO_4 in the Mixture, as SO_3			H_3PO_4 in the Mixture as P_2O_5			HF in the Mixture as F		
	Taken, mg.	Found, mg.	Error, %	Taken, mg.	Found, mg.	Error, %	Taken, mg.	Found, mg.	Error, %
1	2.20	2.24	1.81	10.85	10.89	0.39	1.55	1.50	3.20
2	2.20	2.22	0.90	21.70	21.55	0.69	1.55	1.49	3.90
3	2.20	2.26	2.72	32.55	32.00	1.70	1.55	1.62	4.50
4	4.40	4.31	2.04	43.30	42.08	2.04	1.55	1.48	4.50

TABLE 5—HIGH FREQUENCY TITRATION OF TECHNICAL PHOSPHORIC ACID WITH SODIUM HYDROXIDE AND BARIUM CHLORIDE

Sample A: 6.048 g. of the acid taken as such and diluted to 100 ml.
Sample B: 6.256 g. of the acid taken as such and diluted to 100 ml.

Sample No.	Gravimetric Determination, %		Determination by High Frequency Titrations					
	H_3PO_4 as P_2O_5	H_2SO_4 as SO_3	Vol. of Diluted Acid Taken for Titration, ml.	H_3PO_4 as P_2O_5 (from second break), %	H_2SO_4 found by $BaCl_2$ Titration: Milliequiv. per 100 ml. (a)	H_2SO_4 found by $BaCl_2$ Titration: as SO_3 %	$H_2SO_4+H_2SiF_6$ Milliequiv. per 100 ml. (from first break) (b)	H_2SiF_6 Milliequiv. per 100 ml. (b-a)
A	28.55	1.46	1 ml	28.10	2.10	1.38	3.60	1.50
			1 ml.	28.25	2.00	1.32	3.60	1.60
			2 ml.	27.98	2.15	1.42	3.85	1.70
B	23.15	1.22	1 ml.	22.75	1.85	1.19	2.75	0.90
			2 ml.	22.49	1.80	1.15	2.65	0.85
			2.5 ml.	23.68	1.95	1.24	2.74	0.79

to be practically entirely in the form of sulphuric acid. Hence, by subtracting the content of sulphuric acid thus estimated from the amount of sulphuric+hydrofluosilicic acid obtained from the first break in the high frequency titration curves (Fig. 3), the content of hydrofluosilicic acid can be estimated.

The high frequency titration technique thus provides a convenient method for quick estimation of phosphate, sulphate, fluosilicate and fluoride, if any, in commercial samples of wet process phosphoric acid. Only two separate titrations are required for these estimations: one against 0.1 N caustic soda and the other against barium chloride, and the total time required is 30 to 45 min. The results are also reasonably accurate for plant control purposes.

Acknowledgement

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Biological Treatment of Phenol-Bearing Wastes

By

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A study has been made on the development of a suitable biological process for destruction of phenols with a bacterial culture prepared from garden soil. The effect of temperature, pH and air rate on the phenol oxidation rate has been studied. At a temperature of 37°C and an air rate of 0.2 cft/min./l. a phenol concentration of 1170 mg./l. has been reduced to 5 mg./l. in 10-11 hours.

Rapid industrialization and particularly development of the iron and steel industry have given rise to the establishment of a large number of coal carbonization plants in the different parts of the country. The wastes from these plants normally find an outlet into the nearest stream or river and any pollutional constituent present, unless removed, can contaminate the stream beyond the permissible limits[1]. Among the different pollutional constituents, phenols are prominent in the waste waters of the by-product coal carbonization industry. Their presence is objectionable because of toxicity to fish life and the unpleasant taste and odour they impart to water when chlorinated for potable use. The taste is noticeable even in as high dilution as 1 part of phenol in 750,000,000 parts of water by weight[2].

Source of the Phenolic Wastes

Phenols, cresols, xylenols and many of the polyhydric phenols, obtained from the coal tar processing and gas liquor treatment, are therefore present in the waste waters of coal carbonization industry. Phenols are also found in the wastes of various other industries like the synthetic resin, dyestuffs and rubber proofing, etc.

Treatment of Phenolic Wastes

The methods of treatment of phenol-bearing wastes can be divided broadly into two groups, viz.: (A) those for the recovery and (B) others for the destruction of phenols. In the first group, the different processes are: (*a*) solvent extraction using various solvents like benzol,

butylacetate, tricresyl phosphate, etc.; (*b*) solid adsorbent process using active carbon; and (*c*) vapour phase dephenolization by recirculation of steam counter-current to phenolic liquor and scrubbing the phenol-bearing vapours by caustic soda.

In the second group, for the destruction of phenols, the following processes have been used: (*a*) vaporization of phenolic liquor from coke ovens by quenching of the red hot coke; (*b*) chemical precipitation usng lead acetate; (*c*) oxidation using chlorine, chlorine dioxide, ozone, etc.; and (*d*) biological oxidation.

The biological processes for the destruction of phenol have been employed for the treatment of either the coke oven ammonia still waste liquor or the dephenolized effluents. The phenolic liquor is mixed with a large volume of sewage and treated in the conventional sewage treatment plants. The development of a special bacterial culture for oxidation of phenol has given rise to the bacterial oxidation process in recent years. It was observed that phenols disappear slowly from natural water, which according to Müller[3] depend on bacterial action in the presence of oxygen. The use of phenol as a foodstuff by the bacteria was shown by the increase in the bacterial count during decomposition of the phenol in water. An investigation by Kalabina and Rogowskaya[4] on phenol in pure solutions and in gas works waste waters showed that the decomposition was a biochemical reaction, which depend on temperature, aeration, nutrients, etc. It was demonstrated by Gray and Thornton[5] in 1928 that soil bacteria, when properly cultivated, would decompose phenol. Many species of bacteria such as *Pseudomonas*, *Nocardia*, etc. have been found responsible for the oxidation of phenol.

A study was made in this laboratory on the development of a suitable method for destruction of phenol by the biological process using a bacterial culture prepared from a local garden soil.

Experimental

Preparation of Bacterial Culture: 1 g. of a well-cultivated garden soil was taken in a conical flask to which 100 ml. of a nutrient solution containing 0.1 g. each of potassium dihydrogen phosphate, magnesium sulphate, ammonium sulphate, a trace of ferrous sulphate and 0.05 g. of sodium chloride were added. Air was bubbled continuously through the solution and phenol was added every day in low concentration. Phenol content of the solution was estimated at suitable intervals. At the end of two weeks the first sign of phenol oxidation was noted. Gradually the amount of phenol addition was increased and the oxidation of phenol was followed carefully. A fresh culture was inoculated with the above active culture, and aeration and phenol addition were continued. The process of inoculation with the previous culture containing phenol-oxidizing bacteria was repeated several times till a stable and satisfactory culture was obtained. This culture was used in subsequent experiments for oxidation of phenol.

Determination of Phenol Content: The standard methods for the determination of phenols are the bromination[6], Fox and Gauze's[7] and by 4-amino antipyrine[8]. In these experiments for following the oxidation of phenol, a simple but rapid method developed in this laboratory[9] based on the determination of permanganate value was used. As oxidation proceeded, a very low concentration of phenol was encountered. This method was chosen for determining the phenols content but the results were also checked by the standard methods[6-8].

The various aspects of the phenol oxidation by bacterial culture were studied initially by a batch process. The culture was stabilized by aeration of a solution containing phenol at room temperature in a series of conical flasks. 500 ml. of a solution containing phenol was taken in each flask to which 0.5 g. of potassium di-hydrogen phosphate, magnesium sulphate, ammonium sulphate, a trace of ferrous sulphate and 0.25 g. of sodium chloride were added. The concentration of phenol, maintained low in the beginning, was gradually increased to the desired concentration. The phenol destruction rate was followed by analyzing the solution at regular intervals for the permanganate value. The rate of phenol removal was methodically followed and the corresponding air rate noted. The concentration of phenol studied was in the range of 350 to 1200 mg./l. For each phenol concentration, air rate was varied from 0.2 to 0.02 cft/min./l. of solution in successive runs till concordant results were obtained (Table 1, Fig. 1).

The effect of temperature on phenol oxidation was studied at optimum air rate, viz. 0.1 cft/min./l. of solution at concentration of 360 to 900 mg./l. phenol (Table 2; Fig. 2.).

The effect of pH was not studied in detail as it was observed that the oxidation of phenol was not affected within the range of 7 to 8. However, an higher pH, viz. 10-11, was found not suitable for bacterial oxidation of phenol (Table 3). In all cases when phenol was oxidized completely the pH decreased to 5-6.

The following are the other observations made during the above study: when the phenol was oxidized completely, in addition to the lowering of the pH, the

TABLE 1—EFFECT OF AIR RATE ON BIOLOGICAL OXIDATION OF PHENOL

(Temp. maintained at 37°C)

Air Rate cft/min./l.	Initial Phenol Conc., mg./l.	Phenol Concentration After, hr.								
		½	1 ½	3 ½	5 ½	7 ½	8 ½	9 ½	10 ½	11 ½
0.2	425	315	83	5						
0.1	425	361	240	5						
0.02	425	390	372	271	113	44	5			
0.2	800	770	624	63	5					
0.1	825	807	674	373	5					
0.2	1170	1166	1148	1000	795	610		309	158	5

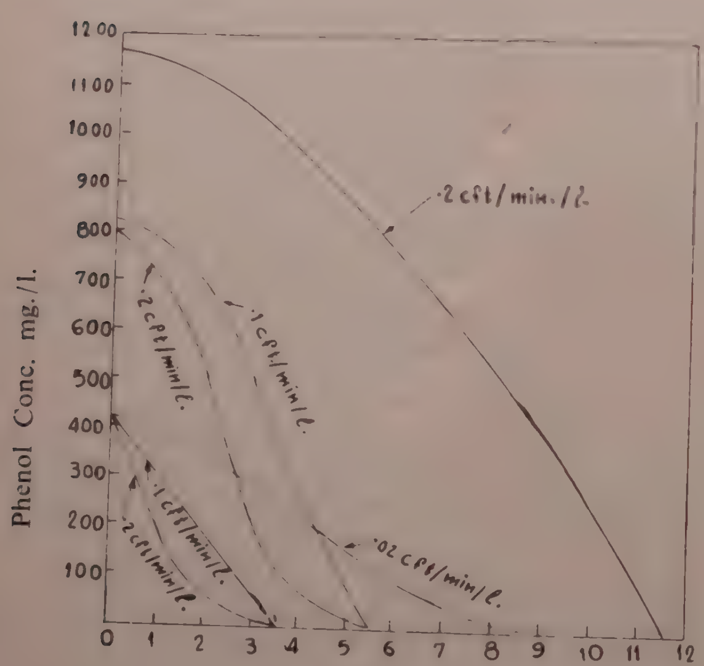

Fig. 1—Effect of Air-Rate on Biological Oxidation of Phenol at 37°C.

solution took a yellow colour and a characteristic sweetish smell was also noticed probably due to formation of some intermediate oxidation products[10]: the bacterial activity was destroyed by sudden increase in phenol concentration, temperature or pH, but the activity could be revived by reducing the temperature, phenol concentration and adjusting pH with continued aeration.

Results and Discussion

The rate of phenol oxidation was found to vary with the supply of air in the system. From Table 1 it is seen that 425 mg./l. of phenol is oxidized completely in 3½ hours at an air rate of 0.2 cft/min./l. of solution whereas the same amount of phenol takes 8½ hours for complete oxidation at .02 cft/min./l. of air rate. At an air rate of 0.1 cft/min./l. oxidation is complete in 3½ hours but its rate is slower in intermediate stages. With higher concentration of phenol, say 800 mg/l. a

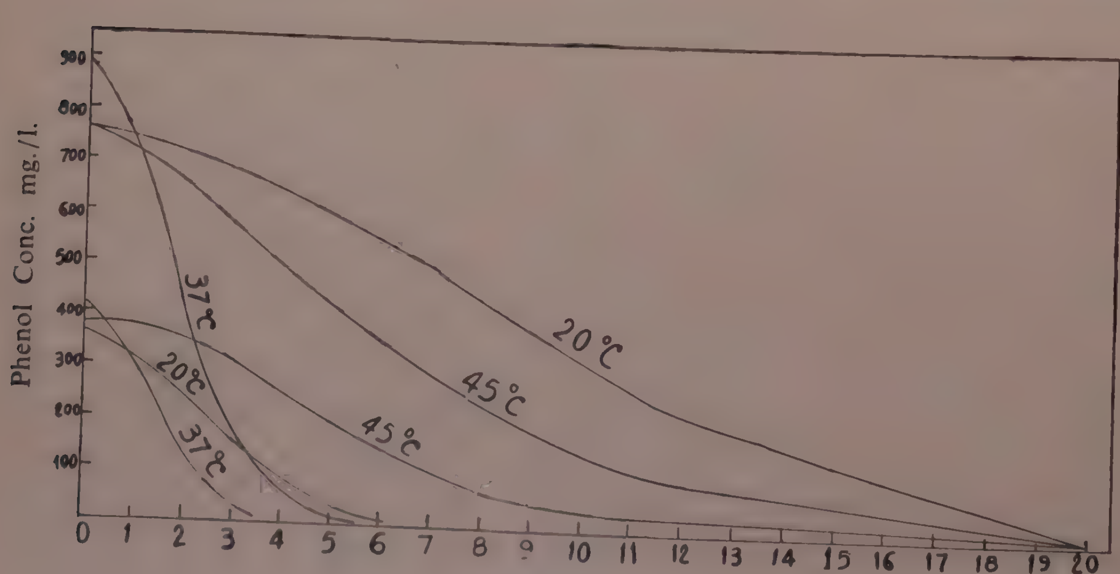

Fig. 2—Effects of Temperature on Biological Oxidation of Phenol (Air-Rate 0.1 cft/min./l).

TABLE 2—Effect of Temperature on Biological Oxidation of Phenol

(Air rate maintained at 0.1 cft/min./l.)

Temperature, °C	Initial Phenol conc., mg./l	Phenol Concentration After, hr.									
		½	1 ½	2	3 ½	4	5 ½	6	8	10	20
20	363			244		77		5			
20	765			698		636		518	454	313	5
45	380			358		262		222	154	29	5
45	765			662		481		356	284	141	5
37	420	363	227		5		5				
37	890	800	641		97						

TABLE 3—Biological Oxidation of Pheonl at Different pH

(Temp. maintained at 37°C and air rate at 0.1 cft/min./l.)

pH	Initial Phenol Conc. mg./l.	Phenol Concentration after, hr.			
		½	1 ½	3 ½	5 ½
7-8	400	382	270	5	
10-11	410	405	405	400	400

similar effect of air rate was observed, the time of complete oxidation being 5½ hours for 0.2 and 0.1 cft/min./l. of solution.

The temperature was also found to have profound effect on the oxidation rate of phenol (Table 2). In the two concentrations of phenol studied, the air rate was maintained at 0.1 cft./min./l. of solution. A temperature of 37°C was found most suitable for phenol oxidation, while an higher (45°C) or lower (20°C) temperature reduced the oxidation rate appreciably.

The effect of pH was not studied in detail but it could be seen (Table 3) that the most desirable pH for phenol oxidation was 7-8. An higher pH (10-11) was not suitable.

The above results indicate that with a suitable bacterial culture prepared from a garden soil in the manner described above, phenol can be destroyed from a phenolic effluent even from a concentration as high as 800 mg/l. in about 5 hours. The external ingredients necessary are the small amounts of nutrients and air. This process will afford an excellent method for phenol removal from effluents without much expenditure.

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Inorganic Transformation of Water-Soluble Phosphates in Some Indian Soils of Varying pH

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Phosphorus fractionation of native and applied phosphates of four Indian soils of varying pH, ranging from 5.3 to 8.4, at different time intervals has been carried out. The native phosphorus is present only in two forms. Acid soils contain high amount of iron phosphates while alkaline (calcareous) soil contains high amount of calcium phosphates. Neutral soil contains both iron and calcium phosphates in comparative amounts. Water-soluble phosphate, when added to these soils, was converted to aluminium, iron and calcium phosphates. Saloid-bound phosphate was least in acid soils, while the alkaline (calcareous) and neutral soils contained comparatively higher amounts of this fraction. The acid soils resulted in the formation of the highest amount of iron phosphates while the alkaline (calcareous) and neutral soils resulted in the formation of highest amount of calcium phosphates. Formation of aluminium phosphates did not follow any such trend. With lapse of time, iron phosphate fraction increased, whereas aluminium phosphate and calcium phosphate fractions decreased. After 7 days' treatment almost all applied phosphate was recovered, but after 105 days there was less recovery of the added phosphate.

Water-soluble phosphates when added to soil are readily converted to relatively less soluble forms. Lindsay[1] *et al.* have reported that plants obtain most of their phosphorus from the newly formed reaction products and not from the fertilizer *per se*.

In order to have a better understanding of the availability of phosphates to crops, it appears essential to measure the discrete forms of phosphates formed in soil after the addition of water-soluble phosphates. With this end in view, a study was undertaken to follow the transformation of applied monocalcium phosphate monohydrate in some Indian soils of varying pH, into various phosphate fractions.

Experimental

Surface (0″-9″) soil samples, ranging in pH from 5.3 to 8.4 used in this study are described in Table 1. Soil samples were air-dried, crushed and made to pass through 2 mm sieve (B.S.S.). 100 g. of each sample were taken in four sets of polythene bottles. Phosphorus was added to each bottle at the rate of 250 μg. P/g. of soil in the form of solution of monocalcium phosphate monohydrate. The volume of added solution was so adjusted that each soil received moisture equal to 50 per cent of its water-holding capacity. Two of the four sets were kept for 7 days and the other two for 105 days. The latter set was weighed occasionally to replenish the loss in moisture. After the specified time intervals, the soil samples were dried in the sun, gently ground and mixed thoroughly. 1 g. of soil was drawn from each bottle for phosphorus fractionation and the analysis was done in duplicate.

Phosphorus fractionation was carried out by the method of Chang and Jackson[2]. Only first four fractions of the method described were included in this study. Fife[3–5] recently proposed a modification over Chang and Jackson's[2] method for determining aluminium phosphate, for its selective delineation, using 0.5 N NH_4F with pH 8.0-8.5 and 16 hours' shaking. Fife's proposed method was compared with the original method[2] using 0.5 N NH_4F with pH 7.0 and 1 hr. shaking. No difference in the extraction of aluminium phosphate by these two methods was observed. Therefore, throughout this investigation the original method[2] was adopted. The chemical analysis of soils was carried

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TABLE 1—CHARACTERISTICS OF SOIL SAMPLES

Location	pH	Coarse Sand	Fine Sand	Silt	Clay	Al_2O_3	Fe_2O_3	Free Iron as Fe_2O_3	Total P_2O_5	CaO
		Per cent								
Netarhat (Bihar)	5.3	2.50	17.50	18.80	61.20	11.66	8.88	5.49	0.063	0.29
Ranchi (Bihar)	6.0	11.62	21.38	20.00	47.00	9.01	5.04	2.29	0.048	0.55
Kanpur (U.P.)	7.1	0.55	63.85	18.60	17.00	3.20	2.74	0.57	0.062	0.59
Coimbatore (Madras)	8.4	24.38	20.02	5.40	50.20	7.07	3.52	0.15	0.111	3.11

out by Piper's method[6], while the mechanical analysis was done by the International Pipette method[7]. Free iron was determined by the method described by Coffin[8]. Soil pH was determined using glass-calomel electrode Cambridge pH meter with 1 : 2.5 soil (air-dry) to water ratio.

For the sake of convenience, N NH_4Cl-extracted phosphorus is reported as saloid-bound-P, 0.5 N NH_4F-extracted phosphorus as Al-P, 0.1 N NaOH-extracted phosphorus as Fe-P, and 0.5 N H_2SO_4-extracted phosphorus as Ca-P. However, the extracted phosphates reported may not be taken entirely specific for these phosphate compounds.

Results and Discussion

Table 2 contains the results of phosphorus fractions of the native inorganic phosphorus in the soil samples used. The data indicates that, in general, phosphorus is present in these soils only in two forms. Iron phosphate is the dominant fraction in Netarhat upland and Ranchi lowland acid soils. Calcium phosphate is the dominant fraction in Coimbatore black soil. Kanpur neutral soil contains both iron and calcium phosphates in comparative amounts. Wright and Peech[9] also reported that iron phosphate comprised the largest portion of the native inorganic phosphorus in some acid soils, of which they carried out phosphorus fractionation. Similarly, MacKenzie[10] observed that calcium phosphate was the dominant fraction in soils above pH 7.4. Aluminium phosphate fraction is present in traces in almost all soils, except Coimbatore black soil. Chang and Juo[11] have reported that aluminium phosphate is usually the least in amount of the three forms, unless the soil is highly fertilized in relatively recent time. Saloid-bound phosphate fraction is not present in any of the soils.

TABLE 2—INITIAL PHOSPHORUS FRACTIONS OF THE SOILS

Soil	Saloid-bound P	Al-P	Fe-P	Ca-P
	μg. P/g of Soil			
Netarhat Upland	Nil	tr	66	15
Ranchi Lowland	Nil	tr	60	24
Kanpur Alluvial	Nil	tr	52	82
Coimbatore Black	Nil	3	15	435

tr=traces

Phosphorus fractions of the soils, 7 days after the application of water-soluble phosphate, are recorded in Table 3. The results show the presence of saloid-bound phosphate fraction in all soils except Netarhat upland acid soil. The presence of this fraction in Netarhat upland soil in traces and in very low amount in Ranchi lowland soil may be due to their high phosphate fixing capacity apparently due to the presence of high amounts of free iron and clay in both these acidic soils.

The formation of aluminium phosphates can be observed in all soils after the addition of water-soluble phosphate. However, these results indicate that there is no definite relation between the pH of the soils and the quantity of this fraction of phosphate formed. Similar results have been reported by Laverty and McLean[12] as a result of their study on the inorganic transformation of added water-soluble phosphate in arable soils with varying pH.

There is an increase in iron phosphate in all the soils after the addition of water-soluble phosphate. Netarhat upland and Ranchi lowland acid soils contain maximum amounts of iron phosphate fraction. These soils are acidic in reaction and contain high amount of free iron, which appears to have reacted with added phosphates

TABLE 3—PHOSPHORUS FRACTIONS AFTER 7 DAYS' TREATMENT AND NET CHANGE IN EACH FRACTION FROM INITIAL SOIL PHOSPHORUS FRACTIONS

(Phosphorus added at the rate of 250 μg P/g. of soil)

Soil	Saloid bound P	Al-P	Fe-P	Ca-P	Net Change in Each Fraction from Initial Soil Phosphorus Fraction: Saloid bound-P	Al-P	Fe-P	Ca-P
	μg P./g of Soil							
Netarhat Upland	tr	46	198	90	Nil	+46	+132	+ 75
Ranchi Lowland	2	47	190	100	+ 2	+47	+130	+ 76
Kanpur Alluvial	44	43	94	200	+44	+43	+ 42	+118
Coimbatore Black	10	53	30	600	+10	+50	+ 15	+165

tr = traces

thereby resulting in the formation of higher amounts of iron phosphates in these soils. The formation of iron phosphate decreased with increase in the pH of the soils.

Calcium phosphate fraction increased in all soils. The highest amount of calcium phosphate fraction formed can be seen in Coimbatore black soil. This soil is alkaline in reaction and calcareous in nature. Calcium present in this soil appears to be most active in reacting with the added soluble phosphate through any of the mechanisms described by Russell[13], thereby resulting in the formation of higher amounts of calcium phosphate in this soil. Kanpur neutral soil also contains calcium phosphate as the dominant fraction as compared to other phosphorus fractions after the addition of soluble phosphate. Kurtz[14] has reported that calcium phosphate complexes are expected in increasing amounts as neutrality is approached. The formation of calcium phosphate fraction decreased with decrease in the pH of the soils.

It is interesting to note that there is an increase in iron and aluminium phosphate fractions even in neutral and alkaline soils after the addition of water-soluble phosphate. Similar observations have been made by Chang and Jackson[15].

Phosphorus fractions of the soils, 105 days after the addition of phosphate, are given in Table 4. The data shows that with the lapse of time from 7 to 105 days, there is a decrease in saloid-bound, aluminium and calcium phosphate fractions, while there is an increase

TABLE 4—PHOSPHORUS FRACTIONS AFTER 105 DAYS' TREATMENT AND NET CHANGE IN EACH FRACTION FROM 7 DAYS' TREATMENT

(Phosphorus added at the rate of 250 μg. P./g. of Soil,

Soil	Saloid-bound P	Al-P	Fe-P	Ca-P	Net Change in Each Fraction from 7 Days' Treatment: Saloid-bound P	Al-P	Fe-P	Ca-P
	μg. P/g of Soil							
Netarhat Upland	tr	40	216	15	Nil	− 6	+18	−75
Ranchi Lowland	tr	38	212	44	− 2	− 9	+22	−56
Kanpur Alluvial	26	35	123	145	−18	− 8	+29	−55
Coimbatore Black	tr	41	35	592	−10	−12	+ 5	− 8

tr=traces

in iron phosphate fraction. The change of aluminium and calcium phosphate fractions into the less soluble iron phosphate fraction with lapse of time seems to be in accordance with the principle of solubility product as reported by Chang and Jackson[16].

After 7 days' treatment almost all applied phosphate was recovered in the form of different fractions extracted but in case of 105 days' treatment less applied phosphate was recovered. This could be due to the formation of "occluded" phosphates with the lapse of time or due to some biological fixation as suggested by MacKenzie[17].

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Studies on the System $(NH_4)_2SO_4$-$CaSO_4$-H_2O

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X-ray and conductometric studies on the system $CaSO_4$-$(NH_4)_2\,SO_4$-H_2O have been made at different temperatures. The presence of syngenite, pentasalt and disalt and their relative stability at different temperatures have been more thoroughly established. In the solid state both syngenite and pentasalt exist at room temperature while disalt at high temperature. In the solution state the existence of pentasalt has been found at 50 and 75°C whereas syngenite has been found at temperatures between 27-75°C.

During the manufacture of fertilizers from the usual components, besides the usual chemical reactions between initial components, many double salts and solid solutions can form between the initial and/or final components to a marked extent.

Under certain conditions, solutions of ammonium and calcium sulphate will deposit three types of double salt viz. ammonium syngenite, dicalcium ammonium sulphate and pentacalcium ammonium sulphate. The salts usually encountered in sulphate plant practice are syngenite and dicalcium salt, which deposit as a hard rock-like mass and have an extremely low solubility in water.

The solidus-liquidus isotherms in the system $CaSO_4$-$(NH_4)_2\,SO_4$-H_2O have been studied by various authors.[1–3] The optical data for three types of double salts[4,5] and

powder diffraction data for two types of double salts e.g. syngenite and pentacalcium salt have so far been published[6–8]. But little is known about their crystallographic properties and thermal stability in the solid state. Similarly very scanty information is available about their existence and stability in the liquid state as well as their mode of formation therein. It seemed that such a study might clarify the conditions of their formation, stability and ready identification, which in turn will have important bearing on the process and quality control.

TABLE 1—FINAL AGREEMENT OF OBSERVED AND COMPUTED Q_{hkl}'s FOR SYNGENITE—$CaSO_4$ $(NH_4)_2$ SO_4 H_2O

Powder Diagram Line	dÅ	I	Q observed	Q Computed	hkl
1	9.900	s	0.0102	0.0102	100
2	6.100	w	0.0268	0.0275	010
3	5.860	s	0.0291	0.0295	001
4	5.234	vw	0.0365	0.0377	110
5	4.970	mw	0.0405	0.0408	200
6	4.735	s	0.0446	0.0440	$30\bar{1}$
7	4.290	ms	0.0543	0.0552	$30\bar{2}$
8	4.128	m (Br)	0.0586	0.0570	011
9	3.852	mw	0.0674	0.0683	210
10	3.620	s	0.0763	0.0763	$10\bar{2}$
11	3.50	s	0.0816	0.0826	$31\bar{2}$
12	3.315	s	0.0910	0.0918	300
13	3.141	w	0.1014	0.1025	$41\bar{2}$
14	3.029	mw	0.1090	0.1068	020
15	2.910	vs	0.1181	0.1164	002
16	2.803	m	0.1273	0.1236	$12\bar{1}$
17	2.685	vvw	0.1387	0.1395	$02\bar{1}$
18	2.583	vw	0.1499	0.1508	220
19	2.497	vvw	0.1604	0.1615	$51\bar{3}$
20	2.400	vvw	0.1736	0.1754	121
21	2.361	w	0.1794	0.1794	102
22	2.231	vvw	0.2009	0.2018	320
23	2.192	vvw	0.2081	0.2072	112
24	2.107	mw	0.2253	0.2261	311
25	2.072	mw	0.2329	0.2318	221
26	2.018	vw	0.2456	0.2403	030
27	1.940	w	0.2657	0.2619	003
28	1.897	m	0.2779	0.2770	031
29	1.850	m	0.2922	0.2930	013
30	1.802	m	0.3080	0.3086	321
31	1.761	w	0.3225	0.3232	411
32	1.718	vvw	0.3388	0.3393	330
33	1.632	vvw	0.3755	0.3755	023
34	1.593	w (Br)	0.3941	0.3947	610
35	1.554	vw	0.4141	0.4133	501
36	1.498	vw	0.4456	0.4461	331
37	1.460	vw	0.4691	0.4695	041
38	1.432	vvw	0.4877	0.4873	402
39	1.397	vvw	0.5124	0.5130	033
40	1.372	vvw	0.5312	0.5318	340
41	1.347	vvw	0.5511	0.5513	601
42	1.311	mw	0.5818	0.5812	024
43	1.273	vvw	0.6171	0.6167	313
44	1.191	vw	0.7050	0.7055	043
45	1.164	vvw	0.7381	0.7379	403
46	1.144	vw	0.7641	0.7650	015
47	1.054	vw	0.9002	0.9005	314

Experimental and Results

Preparation of Samples: Materials used were $CaSO_4$ and $(NH_4)_2SO_4$ of E. Merck and Co. and B.D.H. respectively. $(NH_4)_2SO_4$ was recrystallized from water.

TABLE 2—FINAL AGREEMENT OF OBSERVED AND COMPUTED Q_{hkl}'s FOR PENTACALCIUM SALT—5 $CaSO_4$. $(NH_4)_2SO_4$. H_2O

Powder Diagram Fine	dÅ	I	Q observed	Q Computed	hkl
1	5.98	s	.0279	.0272	200
2	4.00	vw	.0625	.0616	020
3	3.48	ms	.0826	.0819	001
4	3.34	vvw	.0896	.0852	210
5	3.22	vvw	.0962	.0962	$20\bar{1}$
6	3.03	s	.1089	.1116	400
7	2.92	vvw	.1173	.1127	011
8	2.822	s	.1256	.1256	201
9	2.590	vvw	.1491	.1525	$21\bar{1}$
10	2.367	vw	.1785	.1776	220
11	2.325	vvw	.1850	.1817	211
12	2.158	ms	.2147	.2114	$12\bar{1}$
13	2.015	vvw	.2463	.2500	040
14	1.921	mw	.2710	.2703	$40\bar{1}$
15	1.857	s	.2900	.2908	130
16	1.748	vvw	.3273	.3304	002
17	1.712	m	.3412	.3316	230
18	1.672	vw	.3577	.3584	012
19	1.490	vw	.4504	.4508	022
20	1.450	vw	.4756	.4760	$22\bar{2}$
21	1.376	vvw	.5282	.5277	$60\bar{1}$
22	1.344	m	.5536	.5625	060
23	1.274	w	.6161	.6153	601
24	1.255	w	.6349	.6330	132
25	1.165	w	.7368	.7434	003
26	1.146	vvw	.7614	.7596	$11\bar{3}$
27	1.130	vvw	.7831	.7836	150
28	1.095	vvw	.8340	.8353	203
29	1.089	vvw	.8432	.8456	$24\bar{2}$
30	1.078	vvw	.8605	.8603	023
31	1.049	vvw	.9088	.9048	602
32	1.006	vvw	.9881	.9876	450
33	0.956	vvw	1.0942	1.0953	$60\bar{3}$
34	0.9538	vvw	1.0992	1.0976	052
35	0.8637	vvw	1.3405	1.3412	014
36	0.8416	vvw	1.4118	1.4112	$40\bar{4}$

TABLE 3—INDICES OF POWER DIAGRAM LINE OF DI-SALT AND ITS LATTICE PARAMETER CALCULATED FROM EACH LINE POSITION-2 $CaSO_4$. $(NH_4)_2$ SO_4

Powder Diagram Line	θ	2θ	dÅ	I	Sin $^2\theta$	$S=h^2+k^2+l^2$	$\lambda^2/4a^2$	hkl	a (Å)
1	12.855	25.710	3.465	vw	.0495	2	.0247	110	4.901
2	13.905	27.810	3.200	vvw	.0577	3	.0190	111	5.590
3	17.715	35.430	2.532	s	.0925	5	0.185	210	5.663
4	18.960	37.920	2.372	ms	.1056	6	.0177	221	5.792
5	21.980	43.960	2.059	vw	.1400	8	.0175	220	5.825
6	23.250	46.500	1.953	vvw	.1557	9	.0173	300, 221	5.845
7	24.600	49.200	1.851	m	.1733	10	.0173	310	5.845
8	27.030	54.060	1.696	vw	.2065	12	.0172	222	5.875
9	31.365	62.730	1.480	vvw	.2709	16	.0169	400	5.928
10	32.370	64.740	1.440	vvw	.2866	17	.0168	410, 322	5.946
11	36.270	72.540	1.303	vvw	.3500	21	.0167	421	5.962
12	37.395	74.790	1.269	vvw	.3687	22	.0167	332	5.962
13	42.090	84.180	1.150	vvw	.4493	27	.0166	511, 333	5.980
14	57.075	114.150	0.918	vvw	.7045	43	.0163	533	6.037
15	60.270	120.540	0.887	vvw	.7540	46	.0163	631	6.037
16	62.200	124.400	0.870	vvw	.7825	48	.0163	444	6.037
17	72.540	145.080	0.808	vw	.9100	56	.0162	642	6.053
18	74.985	149.970	0.797	vvw	.9328	59	.0161	731, 533	6.071

Ammonium syngenite and pentacalcium salt were prepared by grinding the theoretical amounts of $(NH_4)_2$ SO_4 and $CaSO_4$ $2H_2O$ to a fine powder. These compounds were then intimately mixed and then water was added to make a uniform paste. This was allowed to dry at room temperature for crystallisation. Two samples were thus made, designated as A and B.

Dicalcium salt (C) prepared by the above method was found to break into syngenite and gypsum. The paste prepared by mixing the requisite quantities of finely powdered ammonium sulphate, calcium sulphate and water heated to 80°C was again found to be unstable as soon as it was brought back to room temperature. Hence, it was decided to heat the paste in the high temperature x-ray camera for 6 hours before the experiment and photograph taken *in situ.*

X-ray Analysis: The x-ray diffraction pattern of the samples were recorded in the temperature range 30-100°C in Unicam High Temperature Powder Camera of diameter 19 cm, with Philips x-ray units, PW 1010. $CuK\alpha$ radiation in the nickel filter was used, the x-ray tube running at 40kV with 20 mA. The time of exposure was given 15 hours to each sample. The powder camera was calibrated by taking photograph of pure aluminium wire. The intensities of lines on the x-ray powdered photographs for the phase identification was done by usual method of Hanawalt *et al.*[9]

The different phases present in three samples designated by A, B and C at different temperatures are shown in Table 4.

TABLE 4—IDENTIFICATION OF DIFFERENT PHASES IN THE SAMPLES

Temperature, °C	Identification of Phases		
	Sample A	Sample B	Sample C
27	Syngenite	Pentacalcium salt	Syngenite Gypsum
45	Syngenite	Pentacalcium salt	Syngenite Gypsum
75	Syngenite	Pentacalcium salt	Syngenite Gypsum
80	Gypsum Ammonium Sulphate	Pentacalcium salt	Dicalcium Salt
100	Gypsum Ammonium Sulphate	Gypsum Ammonium Sulphate	Dicalcium Salt

Crystallographic Properties of Three Types of Double Salts: The interplaner spacing and the corresponding Q values $Q_{hkl}=1/d^2$ hkl) for syngenite and pentacalcium salt are listed in Tables 1 and 2 and the same of the dicalcium salt in Table 3. The powder pattern was indexed by Ito's method and the procedure for deter-

mining the reciprocal cell have already been described[10].

(i) Syngenite—$CaSO_4$-$(NH_4)_2SO_4$-H_2O

The direct cell dimension is follows:

a=14.79 Å	α= 90°
b=6.032 Å	β=137°58′
c=8.696 Å	γ= 90°

The crystal belongs to the monoclinic system. The indexed powder pattern showed no evidence of glide planes and screw axes. So the possible space group may be any one of the following P2, Pm, P2/m.

(ii) Pentacalcium Salt—5 $CaSO_4$-$(NH_4)_2SO_4$-H_2O

The direct cell dimension is as follows:

a=8.628 Å	α=90°
b=5.700 Å	β=97°17′
c=3.516 Å	γ=90°

The crystal belongs to the monoclinic system. The indexed powder pattern showed the following systematic extinctions.

1. 0k0 absent when k is odd
2. h00 absent when h is odd
3. h0l absent when h is odd

The space group indicated by these data is $P2_1/a\text{-}c^5/_{2h}$

(iii) Dicalcium salt—2 $CaSO_4$-$(NH_4)_2$ SO_4

The indices and the lattice parameter was determined using the following equation for the cubic pattern.

$$\frac{\mathrm{Sin}^2\theta}{(h^2+k^2+l^2)} = \frac{\mathrm{Sin}^2\theta}{S} = \frac{\lambda^2}{4a^2}$$

Since, the systematic error in lattice parameter "a" decreases as θ increases, the true value "a" was calculated from high angle reflection $d_{6\ 4\ 2}$ found to be 6.053. The crystal, therefore, belongs to the cubic pattern. From the indexed pattern, it is concluded that the di-salt belongs to any one of the following space groups, P23-T^1, Pm3-T^1_h.

It may be noted here that in the case of syngenite, our data of "d" spacings are in agreement with those reported in the literature but we have no equivalents of the lines at d=10.00 and 8.18 as quoted by Coates[7] and A.S.T.M.[8] respectively. Using d=10.0 or 8.18 as h00, it seems difficult to index other lines with an accuracy as high as achieved with 9.9 as h00.

Conductometric Measurements: The nature and number of species present in the solution sta*e with increasing the temperature, was also indicated by a conductometric titration of 20 c.c. of 0.0112 M solution of calcium sulphate with a 0.1 M solution of ammonium sulphate. A well stoppered conductivity cell (30 c.c.) was used in the experiment. The temperature of the thermostat was carefully controlled (±0.01°). Conductivity titrations were made with a Phillips conductivity bridge Model PR 9500 at 1000 cycles/sec. The titrations were repeated and found to be reproducible within the limit of experimental error.

Small but detectable changes in slopes are observed upon additions of one equivalent of ammonium sulphate at the temperature of 27, 45, 50 and 75°C. But one more break is obtained upon additions of 0.2 equivalents of ammonium sulphate both at 50 and 75°C (Fig. 1). The slopes and intercepts are calculated from the equation.

$$K=\alpha+\beta C$$

where K is the specific conductance, C the molar concentration and α and β are constants determined by least square fits over concentration ranges of 0.1 M ammonium sulphate of 0-0.38 ml; 0.56-2.1 and 2.3-3.0 ml for 75 and 50°C and 0-2.1 and 2.3-3.0 ml for 45 and 27°C.

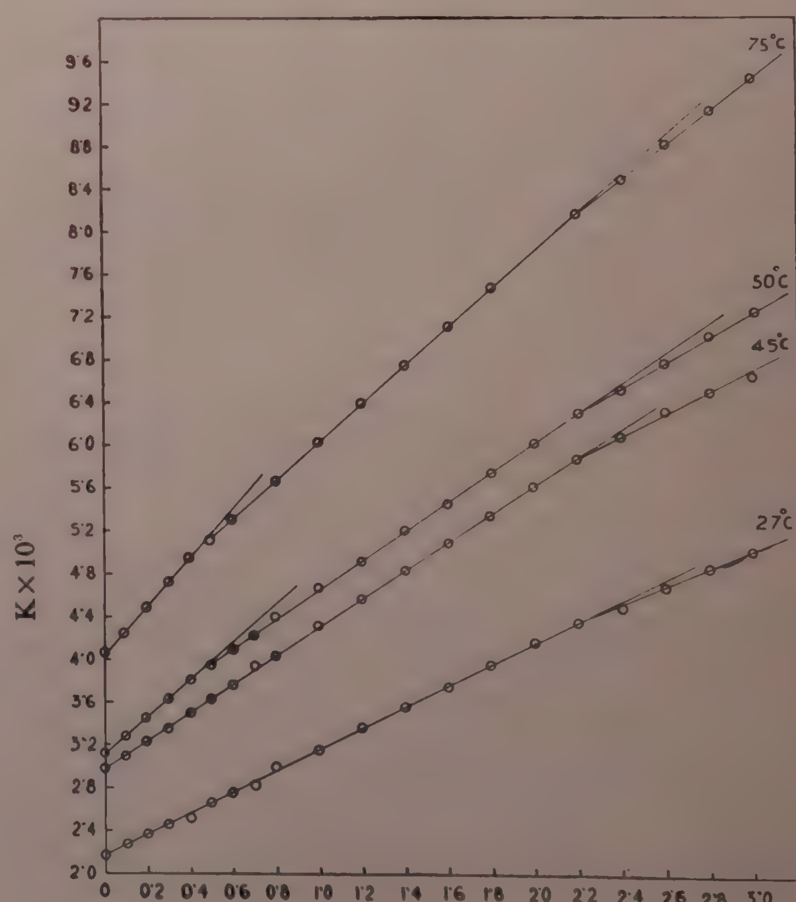

Fig. 1
Ammonium Sulphate (0.1M) Added, ml.

Discussion

With respect to their stability Hill & Yanick[3] have studied the temperature concentration equilibrium of this system. They interpreted the formation of syngenite, pentasalt and disalt in addition to anhydride and gypsum from the study of various isotherms. They have also stated that the various areas indicated in these diagrams, are not areas of stable existence of these salts. The fields for stability and metastability are superimposed in part upon each other.

The thermal stability of the three types of double salts can be interpreted from the phases identified of the three samples at different temperatures (vide Table 5). Syngenite is stable upto 78°C and although pentacalcium salt is formed at the room temperature, its stability increases at first with rise of temperature and at 100°C it breaks into gypsum and ammonium sulphate. Dicalcium salt is unstable below 80°C and breaks into syngenite and gypsum, whereas at 100°C it is quite stable.

TABLE 5

Temperature, °C	Range of Conc., ml. of 0.1M Ammonium Sulphate	$\alpha \times 10^3$	$\beta \times 10^3$	Molar Ratio of $CaSO_4$ to $(NH_4)_2SO_4$
75	0-0.38	4.0417	2.042	5 : 1
	0.56-2.10	4.240	1.780	
	2.30-3.00	4.535	1.646	1 : 1
50	0-0.38	3.131	1.718	5 : 1
	0.56-2.10	3.560	1.318	
	2.30-3.00	3.552	1.240	1 : 1
45	0-2.10	2.969	1.320	1 : 1
	2.30-3.00	4.047	0.882	
27	0-2.10	2.166	0.994	
	2.30-3.00	2.509	0.836	1 : 1

Although it is expected that in the solution state the double salts will be somewhat less stable, it has been observed from conductivity experiments that faint but detectable breaks are observed when the specific conductance is plotted against the concentration of $(NH_4)_2SO_4$ added, at different temperatures. Due to the difficulties involved in performing titrations at higher temperatures, the experiments were carried out within 75°C. It will be observed from Fig. 1 that syngenite is formed at all temperatures, viz. 27, 45, 50 and 75°C, and in addition to syngenite, the pentasalt is detected at 50 and 75°C. Although the formation of pentasalt has been detected in the solid state by x-ray data, at the room temperature the presence of the same could not be detected from conductivity measurements of aqueous solutions.

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Simultaneous Spectrographic Determination of Some Trace Elements in Fertilizer Raw Materials: I—Limestones

By

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Limestone, which constitutes 40 per cent of calcium ammonium nitrate (CAN)—a fertilizer—when added through the fertilizer to the soil, improves its calcium content and structure and the pH of acidic soils. Further, the presence of some micronutrients in the limestone is beneficial for plant metabolism. In the present investigation, a few of the trace elements, viz. lead, copper, gallium, chromium, vanadium, manganese, barium, strontium and titanium, have been estimated in seven Indian limestones. The presence of some other elements in these samples has also been indicated.

In the manufacture of fertilizer CAN, limestone (40 per cent) is mixed with ammonium nitrate (60 per cent) giving the total nitrogen content of about 20.5 per cent. The role of limestone in CAN is two-fold, viz. (1) it acts as a diluent to avoid the hazardous nature of pure ammonium nitrate, and (2) it improves the pH of acidic soils and controls the calcium content and structure of the soil. Moreover, it is well-known that some of the trace elements in limestone may be beneficial and some may be toxic to the plants. Even an element, which is a micronutrient, becomes toxic above a certain limit.

The role of some trace elements, such as copper, manganese, molybdenum, vanadium, zinc, cobalt and boron, has been studied by a number of workers yielding many interesting observations. Recently, Srivastva has studied effects of copper[1] and zinc[2] respectively on the growth characteristics of banana and has given a number of references dealing with utility of copper and zinc as micronutrients. The role of manganese in crop production has been discussed by Moghe[3]. Also, very recently Pillai[4] has discussed the role of trace elements in crop production. Warren and Delavault[5] determined lead, copper, zinc and molybdenum contents of some limestones and related rocks in Ontario, by chemical method. Lead and copper were also determined in limestones by Fiskell[6]. He used Carbamate—EDTA method for copper. In both these methods, not many elements could be determined simultaneously by a single method.

As such it would seem prudent to detect the elements present in some Indian limestones used for agricultural purpose and estimate a number of the trace elements in them. A spectro-chemical method has been used for simultaneous and rapid determination of lead, copper, gallium, chromium, vanadium, manganese, barium, strontium and titanium. A direct-current arc, which is most sensitive for trace elements, was used for the excitation. After trying several elements for use as a single internal standard for the above determinations cobalt was selected for the present work.

EXPERIMENTAL

Description of Samples

For the present investigation, limestone samples from (1) Monda, (2) Dabla, (3) Punjab (4) Nandini, (5) Bisra, (6) Jharbeda and (7) Puranpani, were taken. The first three were received from the Nangal Unit of F.C.I. and others from the Rourkela fertilizer factory. The mineralogical investigation of all the samples, except No. 4, was carried out by Ghosh et. al.[7] It has been

shown[8,9] that sample Nos. 1, 2, 3, 5 & 7 contain dolomite ranging from 4.3 to 12.8 per cent, whereas sample No. 6 is pure calcite.

Procedure

Qualitative Analysis: For the detection of elements present, the samples were oven-dried at about 100°C, and 50 mg. of each was mixed with an equal amount of specpure graphite powder. About 30 mg. of each mixture was packed in duplicate specpure graphite electrodes*, 2 cm long and 6 mm. in diameter, with a crater 4.0 mm deep and 3 mm. in diameter. The counter electrode was 2 cm long and 6 mm in diameter with a conical end. The qualitative analysis was carried out using KCA-1 Russian quartz-glass spectrograph according to an earlier method[10]. The two regions used were 2600-3700 and 2920-4960 Å. The elements detected are given in Table 3.

Quantitative Analysis: For the estimation of trace elements in limestones, 50 mg. of oven-dried samples were mixed with equal amounts of a buffer made of 1 per cent of specpure cobalt powder (internal standard) in graphite powder, and 30 mg of these mixtures were filled in duplicate graphite electrodes to be used as anodes for the two spectral regions given below. During qualitative study of limestones, cobalt was found to be absent in all the samples and as such it could safely be used as an internal standard. For preparation of standards a base was made by mixing Analar/G.R. qualities of calcium carbonate 89.5, silica 5.0, magnesium oxide 3.0, alumina 1.5 and ferric oxide 1.0 per cent respectively. These percentages are based on the average value of the amounts present in above limestones, determined semi-quantitatively by Singhal & Sinha[11]. A mixture of elements to be estimated was prepared by mixing them (mostly in oxide form) in such a ratio that when 10 mg. of this mixture is mixed with 0.990 g. of above base, the highly concentrated standard (No. 1) is obtained. The next standard (No. 2) was prepared by mixing 75 mg. of No. 1 with an equal amount of the base. Similarly three more standards were made to give a set of five. The concentration of various elements in synthetic standards after making correction for trace impurities present in the Analar/G.R. qualities of chemicals, used in preparation of the base, are given in Table 1.

50 mg. of above standards were mixed with same amount of buffer, and 30 mg. of these mixtures were packed in duplicate electrodes, similar to those used for qualitative work.

*From Messrs Johnson & Mathey, England.

TABLE 1—CONCENTRATION OF ELEMENTS IN SYNTHETIC STANDARDS, ppm.

Elements	Std. I	Std. II	Std. III	Std. IV	Std. V
Pb	85	45	25	15	10
Cu	85	45	25	15	10
Ga	80	40	20	10	5
Cr	80	40	20	10	5
V	200	100	50	25	13
Mn	800	400	200	100	50
Ba	845	445	245	145	95
Sr	800	400	200	100	50
Ti	1600	800	400	200	100

TABLE 2—SELECTED ANALYTICAL LINES

Elements	Wave length, Å	Internal Standard Co Wave length, Å
Pb	2833.069	2815.559
Cu	3273.962	3283.462
Ga	2943.637	2989.588
Cr	4254.346	3995.310
V	3185.396	3154.794
Mn	2949.205	2989.588
Ba	4554.042	3995.310
Sr	4607.331	3995.310
Ti	3191.994	3154.794

TABLE 3—QUALITATIVE ANALYSIS OF LIMESTONE SAMPLES

Sl. No.	Limestone From	Elements Detected
1.	Monda	Ca, Si, Mg, Fe, Al, Sr, Ba, Ti, Na, K, Mn, Ga, Cu, V, Pb, Cr & Ni.
2.	Dabla	Ca, Si, Mg, Al, Fe, Sr, Ti, Ba, Na, K, Mn, Cu, V, Ga, Pb, Cr, Ni & Sn.
3.	Punjab	Ca, Si, Mg, Al, Fe, Ti, Sr, Mn, Ba, Na, K, Cu, V, Ni, Pb, Cr & Ga.
4.	Nandini	Ca, Mg, Si, Al, Fe, Mn, Ti, Ba, Na, K, Cu, Ga, V, Sr, Ni, & Cr.
5.	Bisra	Ca, Si, Mg, Al, Fe, Ti, Sr, Ba, Mn, Na, K, Cu, V, Ga, Cr, & Ni.
6.	Jharbeda	Ca, Si, Mg, Al, Fe, Ti, Mn, Ba, Na, K, Cr, Cu, V, Ga, Sr, Pb, Ni & Sn.
7.	Puranpani	Ca, Si, Mg, Al, Fe, Ti, Mn, Ba, Sr, Na, K, Cr, Cu, V, Ga, Ni & Sn.

N.B.—The amounts of elements are roughly in the decreasing order (visual inspection).

TABLE 4—TOTAL CONTENTS OF SOME TRACE ELEMENTS IN SOME INDIAN LIMESTONES
(Expressed as Parts Per Million on Oven-Dry Basis)

Sl. No.	Limestone From	Pb	Cu	Ga	Cr	V	Mn	Ba	Sr	Ti
1.	Monda	8	7	3	2	6	17	31	186	50
2.	Dabla	9	15	5	4	12	22	55	251	79
3.	Punjab	10	9	3	2	9	132	65	tr	105
4.	Nandini	—	13	8	2	3	447	43	tr	209
5.	Bisra	—	13	5	7	20	36	53	138	221
6.	Jharbeda	14	17	4	18	14	122	209	tr	525
7.	Puranpani	—	37	9	39	20	240	200	52	692

tr=traces only
— =absent

Spectrographic analysis was carried out by the earlier method[10] except that in the present case the two regions 2600-3700 and 2920-4960 Å were photographed so that elements, whose sensitive lines fall in the visible region, could be estimated. In addition, an iron spectrum through a 9-step filter was also recorded for plate calibration.

Selected analytical lines are given in Table 2. Using MF-4 Russian Microphotometer, deflections were noted for lines of cobalt and the elements to be determined, and for two selected iron lines through 9-step filter. Clear plate deflection was also noted in every case. The density of each line was calculated and from the calibration curve, corresponding intensity of the lines was noted. Working curves were drawn between the logarithm of ratio between the intensities of lines of the elements and that of cobalt and the logarithm of the concentration of that element in the standards. From these curves the amount of different elements in the limestone samples were noted (Table 4).

Results and Discussion

From Table 3, it will be seen that lead is present in all three samples from Nangal and in one sample (viz. Jharbeda) from Rourkela. Its content was found to be below 15 ppm. Tin was detected in traces only in Jharbeda, Dabla and Puranpani samples and nickel was found in traces in all the seven samples but these two could not be estimated because their lines were too faint.

From Table 4, it is seen that the amount of trace elements differ too much in limestones from different places. Lead, which is present in only four samples, varies from 8 ppm. in Monda to 14 ppm. in Jharbeda sample. Copper is minimum in Monda (7 ppm) and maximum in Puranpani (37 ppm.) sample. While gallium and chromium are least in Monda (3 & 2 ppm respectively) and highest in Puranpani sample (9 & 39 ppm respectively), vanadium is minimum in Nandini (3 ppm) and maximum in Bisra (20 ppm) limestone. Also manganese is found minimum in Monda (17 ppm) and maximum in Nandini (447 ppm), while barium is present only 31 ppm in Monda but it is highest in Jharbeda (209 ppm) whereas strontium is in traces in Punjab, Nandini and Jharbeda but maximum in Dabla (251 ppm). The last element, titanium, is minimum in Monda (50 ppm) and maximum in Puranpani (692 ppm).

A survey of above results shows that most of the trace elements are maximum in Puranpani limestone with the advantage that lead (probably a toxic element) is absent. Also, it can be seen that Monda sample contains minimum amount of most of the trace elements but it also contains lead (8 ppm.).

It is hoped that the work of this nature along with the other works[7-9] already initiated in our laboratory will help in the selection of the fertilizer raw material.

Acknowledgements

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Emission Spectroscopic Estimation of Fluorine in Rock Phosphates

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A method has been devised for estimation of high amounts of fluorine in rock phosphate by employing CaF 5291 Å band head. In observing the behaviour of flourine, it has been noticed that its emission is smoothened in a mixture containing the sample, calcium carbonate, graphite powder, and zinc oxide in the ratio 1 : 1 : 1 : 3. This is further prolonged by taking the sample in a specially shaped electrode—a drilled centre post lower anode —containing calcium carbonate and graphite powder in the ratio, 1 : 1 and the sample thus diluted was taken in the surrounding annular chamber. Cobalt has been found a suitable internal standard in this system, and the accuracy of fluorine estimation by this method is within a relative deviation of 5 per cent.

Rock phosphate is a raw material for phosphatic fertilizers. For assessment of its nature and processing, fluorine determination in it is very important. The chemical method of its estimation is time-consuming and tedious. Compared to it, the emission spectroscopic method is very quick, but the techniques devised so far have much scope for improvement.

In the D. C. arc, fluorine is normally estimated by employing CaF bands. For CaF formation, sufficient Ca^{2+} ions should be present in the arc column, for which the sample is mixed with some calcium salt like calcium carbonate. As CaF bands excite easily (e.p. =2-3.3 volts) and also dissociate easily (the heat of dissociation being 3.3 volts[1]), hence a comparatively cool arc will be most conducive for its emission. But an abundant supply of calcium ions is a much more fundamental criterion for its formation, because fluorine is much more volatile than calcium; hence the reproducibility is decreased if this difference is accentuated and *vice versa.* Ahrens[2] studied the behaviour of fluorine in a specimen of phosphatic rock containing about 0.5 per cent F, and has shown (Fig. 1A) the volatilization curves for several common elements in the phosphatic rock for 1 : 1 dilution of sample with graphite powder, while in Fig. 1B the same in KCl dilution in 1 : 1 ratio. The presence of alkali vapours suppresses the distillation of calcium in early period and when the calcium starts volatilizing later fluorine has already escaped due to its high volatility. Hence, it is evident that high concentration of alkali, if present, will also disturb the accuracy of fluorine determination.

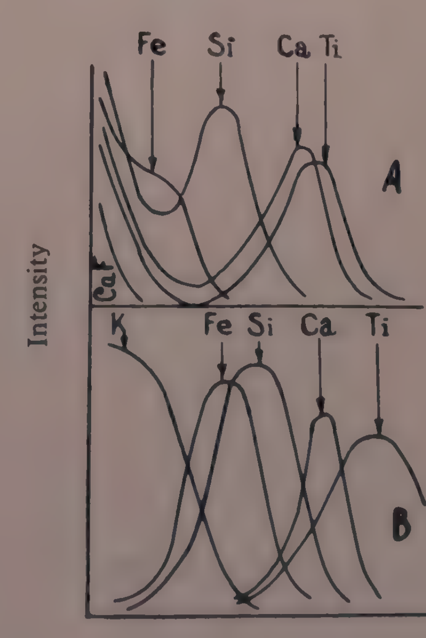

Fig. 1—Selective Volatilization Curves for Several Elements in Phosphatic Rock (after Ahrens). A—without Alkali. B—with KCl.

Seraphim[3] has estimated fluorine in silicates and carefully chosen the matrix, because CaF band emission is fairly sensitive to variation of matrix. He used carbon anode of ¼″ diam. having cavity of 1/8″ diam. ×3/16″ depth, arced at 7 amp. and exposed for 30 sec., after mixing the sample with calcium carbonate in 1 : 1 ratio. Under these conditions, however, reproducibility was poor (15-20 per cent deviation). He achieved some improvement by using CaO 5488 band head as an internal standard, while others[4,5] have used silicon, copper etc. Spindler and Smith[6] achieved some success by mixing their samples (porcelain enamel frits) in the ratio 1 : 1 : 2 as to sample: $CaCO_3$: graphite and arcing at 8 amps, using same type of electrode as used by Seraphim. They also investigated ammonium chloride as buffer and found it unsuitable.

Among the rock phosphates, the apatite variety contains sometime as high as 4-6 per cent fluorine. The difficulty encountered in fluorine determination using CaO band in these cases is that the 5291 CaF band system is very intense and extends over a wider region overlapping CaO 5488 bands particularly in prism optics, thus creating difficulty in measuring the intensity of CaO bands. As such, it is very difficult to correct for background on CaO bands. Keeping these in view, an attempt has been made in the present study to improve upon the fluorine estimation by: (1) finding a suitable buffer for smooth and prolonged evolution of fluorine; (2) devising some method which deaccentuates the volatilization difference between fluorine and calcium; (3) using a suitable internal standard; and (4) minimising the effect of alkali to increase the accuracy.

Experimental

Selection of Buffer: In the d.c. arc analysis, the property of volatilization is the most important factor for controlling reproducibility. In fact, if the distillation rates of internal standard and analysis element are greatly different, reproducibility may be much poorer than when no internal standard is used. It has been pointed out earlier that cool arc is conducive for prolonged CaF emission, but not for initial Ca^{2+} ions formation. The admixture of powdered carbon or graphite with specimen is a common practice for reducing selective volatilization as well as for smooth burning. There are other substances too which have been used successfully as buffers depending upon the nature of estimation. In the present case a natural rock phosphate containing about 4 per cent fluorine was taken as the specimen sample for mixing with various buffers. Various blends were tried for their suitability as an ideal buffer. These were arced at about 8 amp. d.c. taking the sample in ¼″ dia. graphite anode having a cavity of 4 mm dia. ×4 mm depth. The moving plate studies were made for each preparation at an interval of 10 secs. Various blends and their observations are tabulated (Table 1).

Electrode Shape and Size: The dilution 1 : 1 : 3 [Table 1, plate VII (a)] gave the best result as regards smooth emission of CaF band (Fig. 2b), but in plate VII (e) the CaF formation was slightly more intense. This indicated that the initial presence of abundant calcium in the top layer leads to the formation of a profuse quantity of Ca^{2+} ions in the arc column to help more CaF formation. So it was obvious that for best result, (*i*) Ca^{2+} ion should be available from the very beginning and (*ii*) fluorine should come out slowly in the arc column to produce calcium fluoride for which the arc should be comparatively cool. To achieve this condition, Azevedo[7] et. al. used the double chamber electrode for the determination of chlorine in an insecticide powder, with the help of CaCl bands. He mixed the sample with the calcium salt and placed in the 'lower chamber' which was connected to an upper chamber by a small aperature. A small amount of the calcium-salt was then placed in the upper chamber, which is directly exposed to the arc. When arc is struck the arc column is flooded with calcium atoms. As the temperature of the lower chamber increased, chlorine volatilized through the small perforation into the upper chamber and thence to the arc column saturated with calcium. They used very high current (30 amp.) and the calcium fluoride formation was very vigorous which lasted for a short duration (6 sec.) only. A double chamber anode was tried in the present case also but

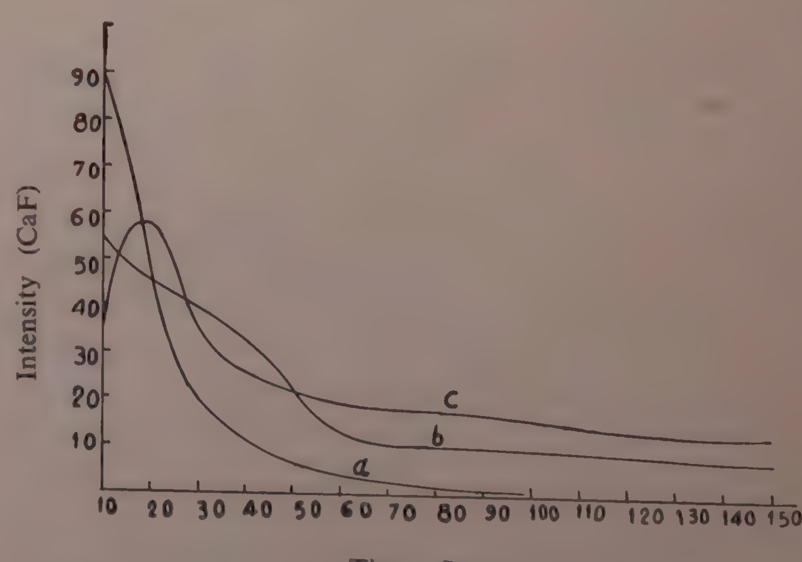

Fig. 2—Behaviour of Fluorine under different conditions.

TABLE 1

Plate No.	Preparation	Observation	Remarks
I	(a) Rock phosphate-1 part (containing 10% Bi_2O_3), Graphite-5 parts. (b) Rock phosphate-1 part (containing 10% $PbCO_3$), Graphite-5 parts. (c) Rock phosphate-1 part (containing 10% $CdCl_2$), Graphite-5 parts.	In these cases BiO, PbO bands were not detected. Bi, Pb & Cd volatilised much earlier than CaF as evident from their atomic lines, Cd being slightly better. Smoothing of CaF and its formation were not upto expectation. CN formation is strong in each case due to high graphite dilution.	Bi, Pb and Cd were tried for internal standard because they are highly volatile like fluorine. The possibility of using BiO and PbO bands were also explored, but without success.
II	(a) Rock phosphate-1 part, Copper oxide-5 parts. (b) Rock phosphate-1 part, Copper oxide-1 part, Graphite-3 parts.	In both the cases, copper supressed calcium. CN bands overlapped the bands of CuO	CuO was tried as buffer as well as i.s.* Possibility of using CuO band as i.s. was ruled out.
III	(a) Rock phosphate-1 part, Li_2CO_3-5 parts.	No formation of CaF at all	$LiCO_3$ buffer was highly unsuitable.
IV	(a) Rock phosphate-1 part (containing 2% ($CdCl_2$), $CaCO_3$-1 part (b) Rock phosphate-1 part (containing 2% $CdCl_2$), $CaCO_4$-5 parts.	In both the cases CaF formation was good but not smooth; formation of CaF in initial period being vigorous. In the latter case CaF was stronger.	$CaCO_3$ was added in these cases with the idea of buffering as well as increasing Ca ion concentration. The blends were unsuitable because of unsmooth CaF emission. Cd was added for trial as i.s.
V	Rock phosphate-1 part (containing 2% $CdCl_2$), Graphite-3 parts.	CaF emission smooth but not upto expectation.	CaF emission was to be further improved upon. Cd was unsuitable in this (as well as in plate IV). It continued for 30 seconds only.
VI	Rock phosphate-1 part, $CaCO_3$-3 parts. Al_2O_3-2 parts, Graphite-4 parts.	Strong AlO band and CaF bands were observed. CaF formation was prolonged. But intensity vs. time curve showed that CaF was stronger in the initial periods and then slowed down, whereas A10 was weak in the initial periods, then became strong and practically remained steady.	A1O band was tried as i.s. but their behaviour was not similar, hence unsuitable.
VII	(a) Rock phosphate-1 part (containing 2% $CdCl_2$), $CaCO_3$-1 part Graphite-1 part, ZnO-3 parts (b) Rock phosphate-1 part (containing 2% $CdCl_2$), $CaCO_3$-1 part, Graphite-2 parts, ZnO-2 parts. (c) Rock phosphate-1 part (containing 2% $CdCl_2$), $CaCO_3$-1 part, Graphite-3 parts, ZnO-1 part. (d) Rock phosphate-1 part (containing 2% $CdCl_2$), $CaCO_3$-1 part, ZnO-4 parts (e) Same as in (d) but with an additional top layer of $CaCO_3$ over the admixture sample.	Among all these five cases in cases of (c) & (d) CaF formation was relatively less, but in the other three cases the CaF formation was rich and emission continued for more than 200 seconds. In the case of (e) CaF intensity was further enhanced probably due to the additional top layer of $CaCO_3$. But in the case of (a) the CaF emission was most smooth. Cd line emission did not also improve in these new matrices; it was there for 30 seconds only.	Here also $CaCO_3$ was still retained for increasing Ca ion concentration but the new substance ZnO was added for its good burning characteristics. The atomic line of Zn could also serve as the internal standard line. From the observations it was concluded that the preparation 1 : 1 : 1 : 3 as to Rock phosphate: $CaCO_3$: Graphite: ZnO was a good base for slow CaF formation and prolongation (Fig. 2b). Atomic lines of Zn were not found suitable for i.s. because it continued vigorously till 50th second only. Cd was also unsuitable, hence finally rejected as i.s.

i.s. = Internal standard.

it was observed that a normal source which had the maximum capacity of supplying 10 amp. current (as in our case) did not develop the required heat in the lower chamber so as to evolve all fluorine from it, as evident from very weak CaF band intensity. But the principle was applied in a different maner. A number of workers like, Harrison & Basseth[8] and Haslar & Dietert[9] used successfully centre post electrodes for estimation of volatile elements. But to suit our particular problem a hole was drilled in the centre post of 3 mm. dia. having a hole of 2 mm. dia. $\times$5 mm. depth, which is about 0.75 mm higher than the edges of the outer annular groove of width 1.2 mm $\times$4 mm depth having 0.5 mm thick surrounding walls. This was shaped from 1/4″ diam. graphite electrode. The counter electrode was also of graphite which was thinned to about 3 mm. dia. The lower centre post hole was filled up with calcium carbonate and graphite powder (1 : 1) mixture. The lower surrounding annular cavity was filled with 1 : 1 : 1 : 3 diluted rock phosphate as in Table 1 [VII (a)]. The shapes of the electrodes are shown in Fig. 3.

Now when the arc was struck, calcium ions from the centre post cavity filled the arc column first. The lower chamber by conduction got heated up with time and released fluorine which slowly and steadily came in arc column to form calcium fluoride readily with the Ca^{2+} ion already present there (as in the case of double chamber). Thus this particular electrode shape was quite elegant in solving the problem created by opposite volatilization behaviour of calcium and fluorine.

Selection of Internal Standard: Volatile metals, like lead, bismuth and cadmium did not suit as internal standard (Table 1, plate no. I). By using the modified electrode and zinc oxide buffer, fluorine behaves similar

Fig. 3—Shape of Electrodes.

to medium volatile elements (Fig. 2c), therefore substances like copper chloride, silver chloride and cobalt chloride were tried as internal standard. About 2 per cent of these salts were added to the rock phosphate sample, buffered in the above manner and fresh moving plate studies were made.

A visual observation of the plates revealed that all the three elements, viz. copper, silver and cobalt, continued to give emission lines for more than 200 secs. along with CaF bands. A closer inspection showed that in the initial period, silver and copper did not behave exectly similar to calcium fluoride. Densitometric calculations were made for the intensity of the internal standard line of Co and CaF 5291 band head. The spectrogram was photographed from 3700 to 5600 Å. The prominent cobalt lines in this region (c.f. M.I.T. table), viz. 3894 Å (1000 R), 3895 Å (300 R), 3995 Å (1000 R) and 3998 Å (200), were found to bahave in a similar way, but from the densitometric point of view Co 3998 Å line was matching in density with the CaF 5291 Å band head line. As no Co-line was available near CaF 5291 Å, the emulsions near the Co-line and CaF band at 4000 and 5300 Å regions respectively were calibrated. This was done by taking an iron spectrum through a nine-step transmission filter. Then two iron lines of equal intensities were chosen for the two regions; densities were measured and the emulsion was calibrated in the usual way by plotting the Siedel function against the log values of filter transmission. The intensities obtained from the calibration were, of course, relative. The background corrections were found necessary for both CaF and Co lines. This was done by taking densitometric readings choosing a clear portion from the spectrum background adjacent to the lines proper. The corrected values for the intensities of CaF band and Co line were determined by substracting the intensity of background from the apparent intensity of these lines.

Curves were plotted with intensity (in arbitrary unit) vs. time drawn upto 100 secs. only (Fig. 4), which showed the closeness of cobalt with CaF in behaviour. For choosing the correct time of exposure, with which precision was directly related, two points were considered. In an ideal case, the ratio of intensities of element and internal standard line should remain strictly constant during successive small periods constituting the total time of exposure. But in practice, although the nature of volatilization remained same, there might be minor variations in the ratios of these small periods of time constituting the total exposure. Now the ultimate intensity of a line was the sum total of the intensi-

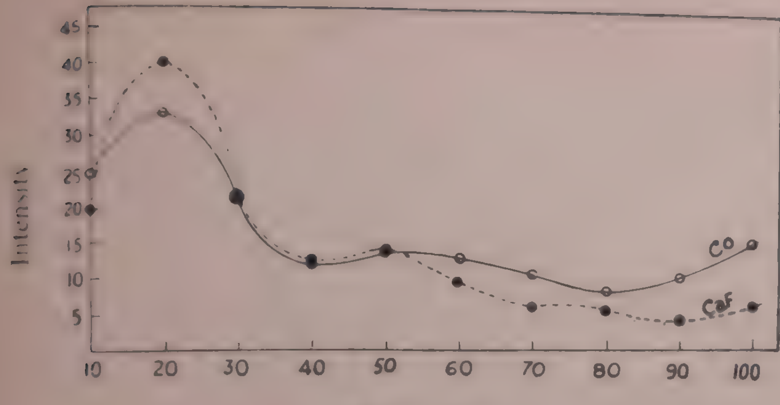

Fig. 4—Behaviour of Cobalt and CaF in special shape Electrodes and 1:1:1:3 Dilution as in Plate No. VII(a) [Table 1].

ties of these elementary periods of composing the exposure time. For choosing the optimum time of exposure both the individual as well as the integrated intensity ratios during the progress of exposure should be considered (Fig. 5).

From the curve (*a*), it was evident that the individual intensity ratio $\frac{I_{CaF}}{I_{Co}}$ attained the constant ratio of 2.1 from an initial value of 1.8 from 20 secs. onwards. Upto the 50th sec. it remained 2.1 and after this the ratio went down to 1.0 in 80 secs. and attained still lower value with time, indicating that CaF emission was comparatively less in the later periods when compared to Co, but its nature of emission remained same.

Curve (*b*) showed the integrated intensities upto the 20th, 30th, 40th, 100th seconds. Here also the intensity ratio $\frac{I_{CaF}}{I_{Co}}$ remained constant upto the 50th sec., and then slowly dropped to 1.7 at 100th sec. So from these two curves, (*a*) and (*b*), the optimum time of exposure should be chosen as 45 secs. One interesting coincidence noticed in this study was that zinc also continued to volatilize vigorously upto 40-45 secs, after which it became weak.

Effect of Alkali Elements: As mentioned by Ahrens[2] and other workers that alkali had much detrimental effect on calcium fluoride due to suppression of Ca^{2+} ions, so the effect of alkali was studied in this new system. For this, two synthetic samples with about 4 per cent fluorine in tricalcium phosphate—one containing no alkali while other 1 per cent sodium—were prepared. (In rock phosphates alkali content is normally within 1 per cent). Moving plate studies for both the samples were made at an interval of 10 secs, after buffering the synthetic samples in the suggested manner and using the modified electrodes. It was encouraging to note that although there was slight variation in the intensity ratios of $\frac{I_{Co}}{I_{CaF}}$ in the individual intervals of 10 secs, the integrated intensity ratios after 40th sec. onwards remained constant within experimental error, which is obvious from Table 2. So alkali effect was less pronounced and was negligible in this system.

Results and Discussion

The nature of calcium fluoride volatilization curve also justified our assumption. In ordinary electrode and normal sample preparation, CaF emission attained peak intensity at the starting of the arc and went down very steep [Fig. 2, curve (*a*)]. Curve (*b*) showed the smoothening effect on CaF due to 1: 1: 1: 3 dilution. Curve (c) showed the effect of the modified electrode in 1 : 1 : 1 : 3 matrix. In the modified system, CaF emission in the beginning was not the maximum, which was attained at nearly 20th sec. and then slightly decreased and remained fairly steady for some time; then it dropped further and continued for a long time. This maximum emission at nearly 20th sec. could be

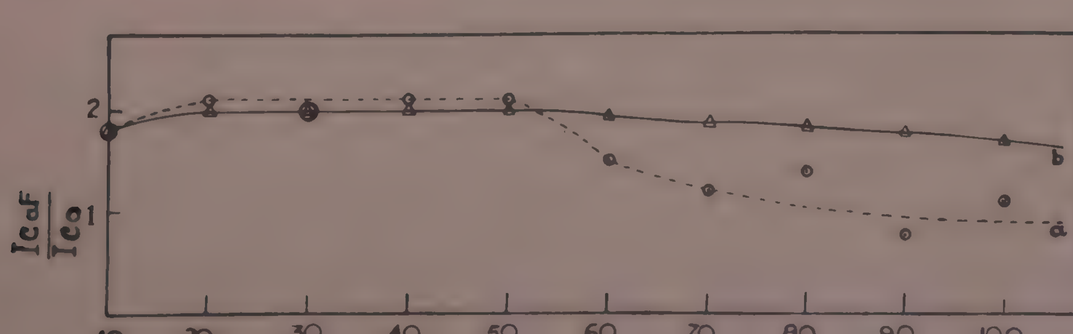

Fig. 5—Individual and integrated Ratios of $\frac{I_{CaF}}{I_{Co}}$ against Time.

(a) Broken line—Individual Ratio.
(b) Continuous line—Integrated Ratio.

TABLE 2

$\frac{I_{Co}}{I_{CaF}}$	0-10 Secs.	11-20 Secs	21-30 Secs	31-40 Secs	41-50 Secs	51-60 Secs	61-70 Secs	upto 10 Secs	upto 20 Secs	upto 30 Secs	upto 40 Secs	upto 50 Secs	upto 60 Secs	upto 70 Secs
No alkali	3.1	3.0	3.8	3.1	4.2	4.6	5.5	3.1	3.0	3.1	3.1	3.3	3.5	3.7
With 1% Na	2.8	3.4	3.5	2.7	3.6	6.3	7.7	2.8	3.0	3.1	3.0	3.1	3.4	3.6

TABLE 3

Spectrograph	Power Supply	Microphotometer	Current, amp.	Exposure Time, Sec.	Plate	Aperture of diaphragm	Developer	Development
Russian make Large glass model KCA-1 with dispersion of about 12 Å/mm at 5200 Å. It has a 3-lens light condensing system.	Indian make Unico D.C. Power supply. Input 230 v.A.C. 50 cycles, Output 150 v-A.C. 10 A.	Russian make Reading/Recording type model M ϕ-4	10 d.c.	45	Afga Yellow rapid	0.5 mm	Kodak 19 b diluted with water in 1 : 1 ratio	3 minutes at 18°C.

TABLE 4

Fluorine in, %				$\bar{X}$ Arithmetic mean of values sample D	Relative deviation $C=\frac{S\times 100}{\bar{X}}$
Sample A	Sample B	Sample C	Sample D		
4.55	3.18	4.55	4.20	4.32	±4.3%
4.33	3.02	4.32	4.50		
4.40	3.34	4.20	4.45		
			4.60		
			4.30		
			4.10		
			4.00		
			4.28		
			4.38		
			4.42		

explained by assuming that fluorine came out from the lower annular cavity due to heat conduction through the centre post. And this optimum condition was reached at about 20th sec.

Various heights for the centre post were tried of which 0.75 mm. above the edges of the lower surrounding walls was found most suitable. As the height of centre post was decreased, it approached the ordinary electrode system, so far CaF emission was concerned. Because in that case the sample came directly in the arc column from the early period of arc excitation. Currents ranging from 8 to 10 amps. were tried and there was little difference in the nature of CaF formation, but 10 amp current gave the best results.

Some natural rock phosphates were taken for its fluorine estimation; for this powdered samples were dried at 100°C for about 24 hours. 2 per cent cobalt chloride was mixed intimately with calcium carbonate powder. Now five synthetic standards were made by taking calcium fluoride in various percentages covering the range of 1-6 per cent of fluorine in tricalcium phosphate base containing a small amounts of ferric oxide, aluminium oxide and silica. These were found present by qualitative spectroscopic and chemical examinations.

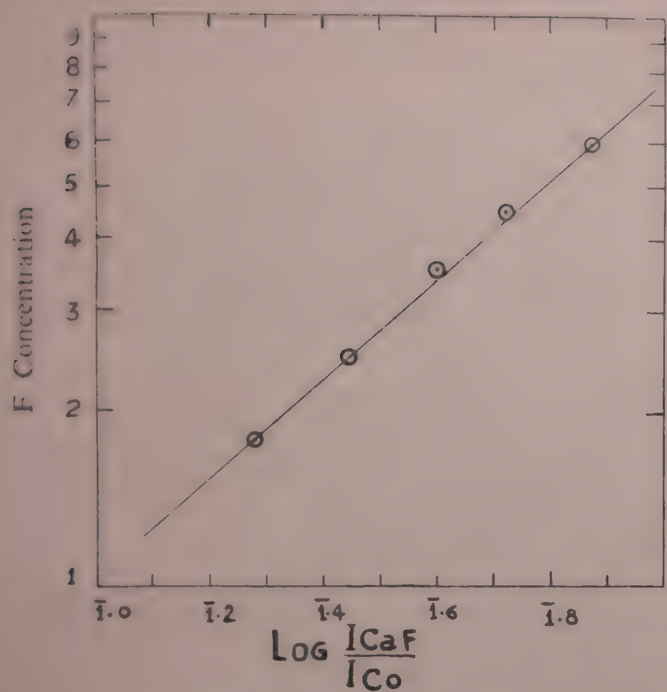

Fig. 6—Working Curve.

All these synthetic samples were mixed in an agate mortar and pestle. These samples were dried in an air oven. All chemicals used were of Analar or guaranteed variety and oven-dried before weighing. Now the unknown samples and the synthetic standards were mixed with calcium carbonate, graphite and zinc oxide in the ratio 1 : 1 : 1 : 3, and they were intimately mixed. These were then loaded in the special electrodes in the surrounding annular chamber and the centrepost hole was filled up with calcium carbonate and graphite mixture (1 : 1). Three arcings were taken for each sample in the same plate along with a nine-step iron spectrum. In another plate, 10 exposures were taken for one sample to find the reproducibility. These plates were developed in identical conditions. The experimental conditions are given in Table 3.

After calculating the intensities as mentioned earlier, the calibration curve was drawn plotting the average of I_{CaF}/I_{Co} values (3 sets) against log of fluorine concentration (Fig. 6). The results obtained for some samples are tabulated below (Table 4).

For sample D, the relative deviation was calculated from 10 sets of different arcings, which was calculated as ± 4.3 per cent.

Acknowledgement

The authors' thanks are to Dr. K. R. Chakravorty, General Manager., P & D Division, for constant encouragement during the progress of the work.

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Studies on the Efficiency of Nitrophosphate and other Nitrogenous and Phosphatic Fertilizers

Part I—Response of Potato in Field Trials*

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In order to compare the relative efficiencies of nitrophosphate—containing 50 per cent water-soluble and 50 per cent citrate-soluble P_2O_5—and other nitrogenous and phosphatic fertilizer combinations on the growth and development of potatoes, a series of field experiments were undertaken. Twelve complex trials in Government farms and twelve simple trials in cultivators' fields were undertaken in six potato growing districts of W. Bengal. The results of these trials clearly indicate that in the case of potatoes, there is no significant difference in efficiency between sulphonitric nitrophosphate and other nitrogenous and phosphatic fertilizer combinations.

Introduction

Among the important shortcomings which have limited the fertilizer production in this country is the shortage of sulphur which is used mainly in the form of sulphuric acid for the manufacture of water-soluble phosphates. Viewed against the present critical situation, this Division of the Fertilizer Corporation of India is working with several agricultural problems for a future fertilizer plan suitable for our economy. One of these is to evaluate the relative merits of nitrophosphate and other nitrogenous and phosphatic fertilizer combinations on the nutrition and yield of different crops. Since the inception of this Division's Fertilizer Trials Station, several field trials have been conducted with different citrate and water-soluble phosphatics,[1, 2] and of late on the basis of these findings a long-term project has been chalked out for testing the merits of nitrophosphates under varieties of agroclimatic conditions prevailing in this country.

So far the use of phosphates was confined mainly to superphosphate containing all the P_2O_5 in water-soluble form. But the raw materials, viz., rock phosphate and sulphur, required for its manufacture are not adequate.

Review of Literature

It is a controversy whether the water solubility of phosphatic fertilizer is the major criterion in their response to crop yields. There are, of course, substantial evidences that water insolubility, in most cases, does not stand against the availability of such fertilizers to plants.

Thorne[3] et al studied the relative efficiencies of nitrophosphates prepared by different processes and found these to be at par with triple superphosphate. In the U.S.A. Rogers[4] showed that in the case of cotton maize and cereals phosphorus of nitrophosphates was as effective as that of triple superphosphate or commercial ammoniated mixtures. Turchin[5] et al concluded from their experiments under the soil conditions of Ukraine (USSR) that 50 per cent water-soluble P_2O_5 is all that is required to make the nitrophosphates effective and keep their efficiency at par with superphosphate. Dicalcium phosphate was sufficiently soluble to maintain an adequate supply of $H_2PO_4^-$ ions to the growing plants and more so in acidic soils. Barbier[7] noted that 1-2 mg/l. of phosphate (P_2O_5) was all that was necessary for optimum nutrition of the plants, and the solubility of dicalcium phosphate being 20-100 mg./l. it was as good a source of P_2O_5 as superphosphate

*Based on the First Report of Fertilizer Field Trials in W. Bengal Rabi Crop 1965-66, Fertilizer Trials Station, P & D Division, FCI Ltd., Sindri, Bihar, 1.4.66. This study was carried out in collaboration with the Directorate of Agriculture, W. Bengal.

for all practical purposes. There are evidences that the availability coefficient of phosphorus in calcium metaphosphate approaches that of concentrated superphosphate in acid to neutral soils[8]. It compared favourably with concentrated superphosphate in a large number of trials with cotton, corn, wheat and legumes in the South-East and Middle West of the U.S.A.[9] In the old established rice fields of France with soils low in calcium, water insolubility of phosphates was never a major factor in increasing crop yields. Similar observations were made in Burma and Vietnam[10]. In Ceylon, no appreciable difference in the response of rock phosphate, ordinary and concentrated superphosphate etc. was obtained[11]. Ground rock phosphate and superphosphate were found to be at par in case of paddy in acid and sandy soils of Ceylon[12].

In acid to near-neutral soils and in crops having longer growing seasons, water-insoluble forms of phosphates are not inferior but even superior to the water-soluble forms which in turn seems to be important in short duration crops and in alkaline soils[13–18].

Terman[11] observed that when mixed with the soils, crop response tends to be similar to fine water and citrate-soluble phosphates and the efficiency of the latter tends to increase with increase in surface area of the granules. From a number of trials, Russell[20] concluded that nitrophosphates containing 40 per cent water-soluble phosphorus would have universal applicability and those with 10 per cent water-soluble phosphorus would be effective for soils fairly high in phosphorus.

In India, a large number of trials have been conducted to determine the relative merits of different varieties of citrate- and water-soluble phosphatic fertilizers. At C.R.R.I., Cuttack[21] and in most of the model agronomic experiments[22], conducted under the auspices of ICAR water-insoluble forms have been found to be as good as the water soluble forms of phosphatic fertilizers. Further, experiments at Burdwan[23], Pattambi[24, 25], Ponnampet[26], Mangalore[27–30], Aduthurai[31–33], Ambasamudram[34, 35], Pusa[36] and Sabour[37] with different crops also corroborate the above findings.

At Hyderabad, ODDA nitrophosphate was at par with superphosphate for rice in both calcareous, phosphate deficient, black clayey soils and red sandy loams[38]. Ray Chowdhury[39] opined that generally for acidic and lateritic soils, dicalcium phosphate or any other citrate-soluble phosphate was universally recognized as a good source of phosphatic fertilizer. Using tracer technique, Dutta[40] noted that in calcareous soils phosphate uptake was more from the citrate-soluble dicalcium phosphate than from any other soluble phosphate. Soluble phosphates, however, showed a higher trend in uptake in black cotton soil though the uptake as a whole was very low (0.6 to 4 per cent). In case of wheat, labelled nitrophosphates (PEC), superphosphate and dicalcium phosphates were tested using Mangalore and Karnal soils. In the case of Mangalore soils which was acidic in reaction, nitric phosphates were found to be better utilized by the wheat plants. The same fertilizers were tested in the case of rice using four different soils viz., from Andhra Pradesh, Kerala, Assam and Bihar. It was found that the percentage utilization of phosphorus from nitrophosphate and dicalcium phosphate was as much as from superphosphate in case of acidic soils of Kerala and Assam while superphosphate was distinctly superior in the other two soils[41].

The present set of trials was undertaken to evaluate the relative efficiencies of nitrophosphate and other nitrogenous and phosphatic fertilizer combinations in encouraging the growth and yield of potatoes.

TABLE 1—Analysis of Soil Samples (on oven-dry basis)

Name of the Farm	Organic Carbon, %	Total Nitrogen, %	Total P_2O_5, %	Total K_2O, %	pH
1. Burdwan Farm	0.300	0.054	0.085	0.159	5.5
2. Memari Farm	0.733	0.051	0.152	0.175	5.8
3. Sainthia Farm	0.390	0.042	0.033	0.094	6.4
4. Bolpur Farm	0.355	0.039	0.031	0.125	6.2
5. Susunia Farm	0.315	0.040	0.033	0.125	7.4
6. Sonamukhi Farm	0.570	0.042	0.066	0.214	6.3
7. Singur Farm	0.773	0.050	0.227	0.325	6.1
8. Adisaptagram Farm	0.458	0.048	0.131	0.313	6.7
9. Gaighata Farm	0.495	0.051	0.053	0.159	6.2
10. Nokphul Farm	1.043	0.057	0.053	0.434	6.6
11. Nakashipara Farm	0.555	0.049	0.074	0.313	7.5
12. Kaliagaunj Farm	0.623	0.053	0.080	0.225	7.1

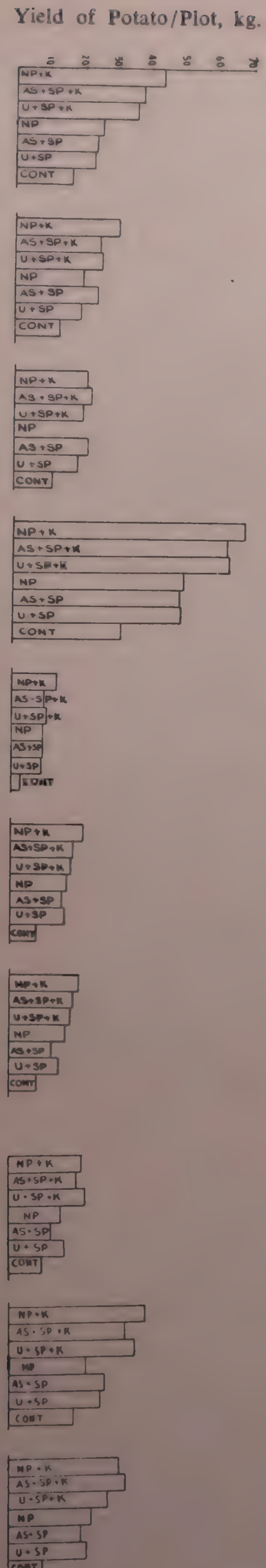
EXPERIMENTAL

Programme of Work

To begin with the programme of extensive fertilizer field trials, twenty-four experiments were designed and carried out in 1965-66 in W. Bengal, using potato as the test crop. Out of these trials, twelve were of complex type while the rest were simple.

The total area of W. Bengal is 34,214 sq. miles and is divided into two natural divisions, viz.: (1) Himalayan region comprising the districts of Darjeeling, Jalpaiguri and Cooch-Behar; and (2) plain comprising the districts

Fig. 1—Map of W. Bengal giving locations of the Trial Plots both in Government Farms and Cultivators' Plots.



Sainthia Fig. 1

Susunia Fig. 2

Sonamukhi Fig. 3

Burdwan Fig. 4

Bolpur Fig. 5

Kaliganj Fig. 6

Gaighata Fig. 7

Nokphul Fig. 8

Memari Fig. 9

Nakashipara Fig. 10

of Hooghly, Howrah, 24 Parganas, Calcutta, Burdwan, Birbhum, Bankura, Purulia, Midnapur, Nadia, Murshidabad, Malda and West Dinajpur (Fig. 1).

A longitudinal strip of laterite soil runs through the south-western parts of Midnapur, Bankura, Burdwan, Birbhum and also some parts of Malda and West Dinajpur. The whole of the districts of Hooghly, Howrah, Nadia, Murshidabad and the rest of Burdwan and considerable parts of 24 Parganas, Jalpaiguri and Cooch Behar and some parts of Midnapur, Bankura, Birbhum, Malda and West Dinajpur contains new alluvial and or old alluvial soils. Near the sea coast in the districts of Midnapur and 24 Parganas there are some saline areas. Parts of Darjeeling, Jalpaiguri and Cooch Behar are composed of forest and hill soils.

The climate of W. Bengal varies mainly with the periodicity of winds. During the monsoon period (June to September) the climate is tropical with high humidity.

The following six districts were selected for conducting the present set of trials: Burdwan, Hooghly, Birbhum, Bankura, 24 Parganas and Nadia.

Site Selection and Land Preparation

While selecting the sites, for conducting the trials, due precaution was taken to avoid drains or ditches and big trees by the sides of the plots. From the previous crop history of all the plots, it appeared that the plots were uniform in respect of fertility, drainage etc. In all, 12 Government farms and 12 cultivators' fields from the above six districts were selected.

All lands were opened just after the harvest of the preceding crop. In the green manured plots, the crop was ploughed during monsoon and left as such until it was ploughed in September. During the final land preparation of the experimental plots, local methods were given preference over the improved ones. Well rotten cowdung at the rate of 150 mds./acre was uniformly incorporated in soil at final ploughing.

Characteristics of the Seed Variety

In all the trials, the Royal Kidney Variety of potato—which is highly responsive to fertilizers and high yielding and medium in duration—was used. The following are its other characteristics: (*i*) *Habit*—Medium tall, open, spreading and medium in vigour; (*ii*) *Foliage*—Stem pink, wing slightly wavy at the top, leaves drooping, secondary leaflets pointing upwards, leaflets medium green and dull; (*iii*) *Flower*—absent, stalks short and buds small; (*iv*) *Tuber*—Large to medium smooth white coloured cylindrical often sharply narrowing down towards heel, eyes fleet, eyebrows slightly curved, flesh colour pale yellow, and (*v*) *Stolons*—short, white.

Both the keeping and cooking qualities of the variety are good. It is immune to virus 'C' and appears to be rather resistant to common scab; but it is susceptible to blight diseases.

Fertilizers Used

The following fertilizers were used: (1) nitrophosphate, (2) ammonium sulphate; (3) urea; (4) superphosphate, and (5) potassium sulphate.

These fertilizers were tested in the laboratory before application. Except nitrophosphate, the rest of the above are well-known to the Indian Farmers. The chemical composition of nitrophosphate produced by the FCI Ltd. Trombay Unit, is given below (Table 2).

TABLE 2—CHEMICAL COMPOSITION OF NITROPHOSPHATE (grade 12.9-12.9-0)

Formula	Composition, %
1. NH_4NO_3	30.2
2. $(NH_4)_2HPO_4$	10.6
3. $CaSO_4$	28.1
4. Mg CO_3	1.6
5. $CaHPO_4$	14.3
Ammonium Nitrogen	7.5 (58% of the total N)
Nitrate Nitrogen	5.4 (42% of the total N)
Total P_2O_5	13.0
Citrate soluble P_2O_5	50-70% of the total P_2O_5)
Water soluble P_2O_5	30-50% of the total P_2O_5)
CaO	18.0

Calcium nitrate content of the product will be about 2.5 per cent.

Rates of Application: All the fertilizers were compared on equal nitrogen, phosphorus and potash basis. Averaging out the different situations of the trial sites, the rates of nutrient applications were fixed at—100 lbs. N, 100 lbs. P_2O_5 and 100 lbs. K_2O per acre.

Statistical Design and Procedure

Since there were altogether 14 treatment combinations including the control (receiving no fertilizers), the experiment was conducted using randomized block design.

Lay-out: After the final preparation of the land, the laying out of the experimental area was completed. Gross plot size was 44′×10′ with 6 rows per plot and 66 numbers of hills per row. The row to row distance was 20″. Provisions for irrigation and drainage were maintained by laying out 2½′ channels in between the blocks.

Application of Fertilizers: The entire quantity of fertilizers was uniformly placed in trenches dug beforehand and thoroughly mixed with the soil (Tables 3A and 3B).

Seeds: Tubers were cut to get 1½ oz. seed pieces taking care that there was at least one eye in each seed piece; these were then treated with agallol before final planting.

Planting: Planting for each experiment was completed in the same day. Seed pieces were put in the trenches keeping a fixed spacing of 8 inches between the seeds. Seeds were then covered with fine soil making small ridges.

Irrigation: Irrigation varied according to local conditions. Since all the sites had adequate irrigation facilities the crop did not suffer from drought.

Plant Protection Measures: Proper preventive measures were taken against insect, pest and fungal attacks. Frequent sprayings of Folidol E-605 and copper fungicides were done as demanded by local conditions.

Harvesting: Harvesting was done when the tubers were fully matured allowing two border rows and an equivalent area from the other two border ends as discards in each plot. Yield records were taken right on the field and tuber samples were collected for laboratory analysis.

Analytical Methods: For the determination of N, P and K in the plant material, the microdigestion method of Yuen and Pollard[42] was followed. Phosphate in the plant material was determined by the molybdenum blue—amino-naphthol sulphonic acid method of Yuen and Pollard[43]. Total nitrogen was determined by the Nessler's method as modified by Yuen and Pollard[44]. The methods used for other estimations were those described by Piper[45].

Results and Discussion

Complex Trials (*Table* 4, *Fig*. 2): Statistical analysis of the tuber yield data clearly indicates that the significant differences observed in the yields are due to the different fertilizer treatments.

In all the 12 experiments there was, in general, no significant difference in tuber yields from NP+K, AS+SP+K and U+SP+K treatments at the 5 per cent level of significance. Although not significant at the 5 per cent level, NP+K was apparently superior to AS+SP+K and U+SP+K in increasing yield of potatoes at Burdwan, Susunia, Kaligunj and Gaighata farms. At Sainthia and Bolpur, NP+K was, however,

significantly superior (at the 5 per cent level) to all the other treatments.

When NP alone was compared with AS+SP and U+SP on equivalent nutrient basis, it was observed in general, that there was no significant difference within these three different sources in increasing the yield of potatoes.

These observations clearly indicate that in case of potatoes, nitrophosphate, when compared with ammonium sulphate+superphosphate and urea+superphosphate on equal N and P_2O_5 basis, is by no means inferior under normal conditions. The above results corroborate the findings of Thorne et al[3], Rogers[4], Venkateshwarlu et al[38], Kamath[44], etc.

Single nutrient applications resulted in considerable lower yields. As a source of nitrogen no significant difference in tuber yields was observed between ammonium sulphate and urea in almost all the centres.

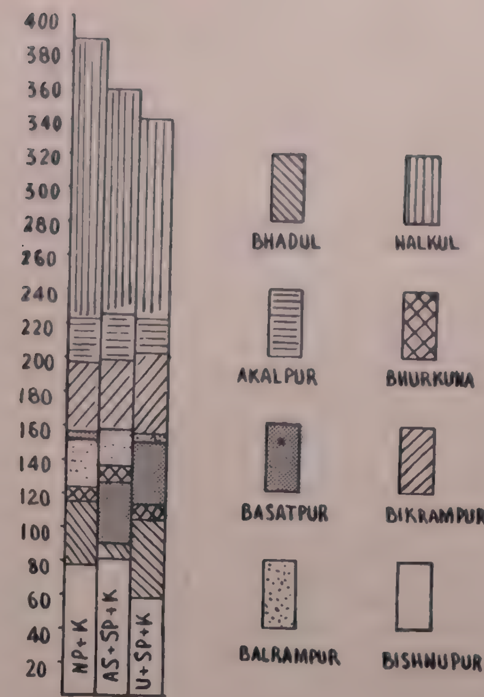


Fig. 3

TABLE 3A—Details of Fertilizer Treatments in Govt. Farm

No.	Abbreviations	Treatment Combinations	lbs. of Nutrient/acre			Amount of Fertilizer, kg/plot				
			N	P	K	NP	AS	U	SP	K
1.	N+PK	Nitrophosphate+Potassium Sulphate	100	100	100	3.55	0	0	0	1.09
2.	AS+SP+K	Ammonium Sulphate+Superphosphate+Potassium Sulphate	100	100	100	0	2.23	0	2.87	1.09
3.	U+SP+K	Urea + Superphosphate + Potassium Sulphate	100	100	100	0	0	1.02	2.87	1.09
4.	NP	Nitrophosphate	100	100	0	3.55	0	0	0	0
5.	AS+SP	Ammonium Sulphate+Superphosphate	100	100	0	0	2.23	0	2.87	0
6.	U+SP	Urea+Superphosphate	100	100	0	0	0	1.02	2.87	0
7.	SP+K	Superphosphate+Potassium Sulphate	0	100	100	0	0	0	2.87	1.09
8.	AS+K	Ammonium Sulphate+Potassium Sulphate	100	0	100	0	2.23	0	0	1.09
9.	U+K	Urea+Potassium Sulphate	100	0	100	0	0	1.02	0	1.09
10.	AS	Ammonium Sulphate	100	0	0	0	2.23	0	0	0
11.	U	Urea	100	0	0	0	0	1.02	0	0
12.	SP	Superphosphate	0	100	0	0	0	0	2.87	0
13.	K	Potassium Sulphate	0	0	100	0	0	0	0	1.09
14.	Control		—	—	—	—	—	—	—	—

TABLE 3B—Details of Fertilizer Treatments in Cultivators' Plots

No.	Abbreviations	Treatment Combinations	lbs. of Nutrient/acre			Amount of Fertilizer, kg/plot				
			N	P	K	NP	AS	U	SP	K
1.	AS+SP+K	Ammonium Sulphate+Superphosphate+Potassium Sulphate	100	100	100	0	7.3	0	0.45	3.6
2.	NP+K	Nitrophosphate+Potassium Sulphate	100	100	100	11.7	0	0	0	3.6
3.	U+SP+K	Urea+Superphosphate+Potassium Sulphate	100	100	100	0	0	3.4	9.45	3.6

TABLE 4—AVERAGE YIELD OF POTATO TUBER FOR EACH TREATMENT AT DIFFERENT FARMS, KG/PLOT
(Each figure represents an average of three replicates.)

Treatments	Sainthia	Susunia	Sonamukhi	Burdwan	Bolpur	Kaligung	Gaighata	Nokphul	Memari	Nakashipara
NP+K	43.16	30.45	21.50	68.73	13.25	21.28	20.70	21.90	40.16	32.50
AS+SP+K	37.33	24.85	22.90	63.50	9.95	18.20	18.75	20.00	34.00	34.25
U+SP+K	35.70	25.35	20.30	64.00	10.15	18.00	18.00	22.65	37.33	29.35
NP	25.20	19.75	19.30	50.35	9.15	16.45	16.45	15.65	22.66	24.60
AS+SP	23.70	24.35	21.90	49.10	8.00	15.56	12.71	12.10	28.50	21.00
U+SP	23.16	19.35	18.50	49.50	9.25	16.00	14.91	16.35	27.16	22.50
AS+K	26.43	19.25	21.10	49.00	6.22	15.90	13.28	13.60	26.66	18.75
U+K	23.13	20.75	15.60	49.75	7.00	15.86	10.50	17.12	22.33	15.25
SP+K	21.50	14.05	12.60	47.56	6.00	13.86	14.11	11.22	27.66	13.35
AS	22.90	20.30	13.80	43.90	5.50	12.71	12.46	15.00	19.66	13.60
U	21.73	17.75	15.60	42.55	6.00	13.00	9.45	11.00	22.00	14.50
SP	18.39	18.55	10.50	40.05	5.25	10.85	11.16	8.15	18.66	10.00
K	20.73	14.80	13.30	15.33	4.60	10.23	10.10	8.60	22.66	9.55
O (Control)	16.63	13.12	11.50	32.05	2.50	7.80	8.05	9.65	19.00	9.75
'F' value of the treatments	28.2*	4.8***	7.91***	10.8***	12.12***	5.2***	20.16***	11.95***	7.80***	30.6***
'F' value of the blocks	90.00**	3.50	0.985	1.44	3.072	1.61	0.253	0.085	3.47*	0.90
C.D. at the 5% level	4.12	4.67	4.61	8.47	2.44	4.48	2 44	4.18	7.056	4.38

*Significant at 5% level
**Significant at 1% level
***Significant at 0.1% level

TABLE 5—AVERAGE YIELD OF POTATO TUBER FOR EACH TREATMENT AT DIFFERENT SITES, KG/PLOT

Treatment	Nalikul Hooghly	Bhadul Bankura	Akalpur Birbhum	Bhurkuna Birbhum	Basatpur Burdwan	Bikrampur Nadia	Bishnupur, 24-parganas	Balarampur Hooghly
NP+K	386.5	122.0	220.0	120.5	154.5	194.0	76.4	152.0
A/S+S/P+K	355.0	88.0	222.0	134.0	126.0	194.3	78.3	154.0
U+S/P+K	339.0	103.5	220.0	111.5	148.5	203.5	55.9	153.5

In general potatoes seem to respond similarly to N, P_2O_5 and K_2O, when applied singly. Control plots produced lowest yields in almost all the centres.

Simple Trials (*Table* 5, *Fig.* 3): The results clearly indicate that there was no consistent significant difference between NP+K, AS+SP+K and U+SP+K treatments in increasing the yield of potato tubers in most of the trials. At Nalikul, Bhadul and Basatpur NP+K produced higher tuber yields than the other equivalent treatments. At Akalpur, the difference within the three treatments was almost insignificant. At Bhurkuna and Bishnupur NP+K was slightly inferior to AS+SP+K but was superior to U+SP+K. At Bikrampur and Balarampur, however, NP+K was slightly inferior to both AS+SP+K and U+SP+K.

It can be generalized from the above findings that under the cultivators' field conditions of West Bengal the performance of nitrophosphate (containing 50 per cent citrate soluble P_2O_5 and 50 per cent water soluble P_2O_5) as a source of N and P_2O_5 will be similar to any other popular source of N and P_2O_5 in the case of potatoes.

Acknowledgements

Thanks are due to Dr. K. R. Chakravorty, General Manager, and Sri A. K. Roy, Additional Superintendent, Planning & Development Division, FCI Ltd., Sindri, Dr. H. K. Nandi, Director of Agriculture, West Bengal, Sri S. Sarkar, Regional Officer (Fertilizer), Directorate of Agriculture W. Bengal, for their keen interest in this work. Sri Sarkar was associated directly with the work. Thanks are also due to all project Executive Officers, Subject Matter Specialists, Block Development Officers, Agricultural Extension Officers, Assistant Farm Managers, Gram Sevaks and the cultivators, associated with these trials, for their timely help in all matters.

Studies on Cobaltic Biuret Complex

By

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It is evident from the spectrophotometric and conductometric studies on the interaction of hexamine cobalt^{3+} chloride and biuret at pH 1.6, that biuret cobalt^{3+} complex is formed in the ratio of 3 : 1.

Earlier workers reported the formation of metal chelate complexes with biuret as ligand[1-4]. According to Nawak[2] et al the photocolorimetric detection of biuret in commercial urea can be made by the Nickel-Complex method in the region of 455-465 mμ In our earlier communication[5], a method for the estimation of biuret in commercial urea has been developed by forming a coloured complex with cobalt salt in presence of excess of alkali. In that process cobaltous chloride has been oxidized *in situ* by 30 per cent hydrogen peroxide.

In the present investigation hexamine cobaltic chloride has been taken and reacted with biuret at pH 1.6. Spectrophotometric and conductometric studies show evidence that a complex is formed in the ratio Co^{3+}: biuret as 1 : 3.

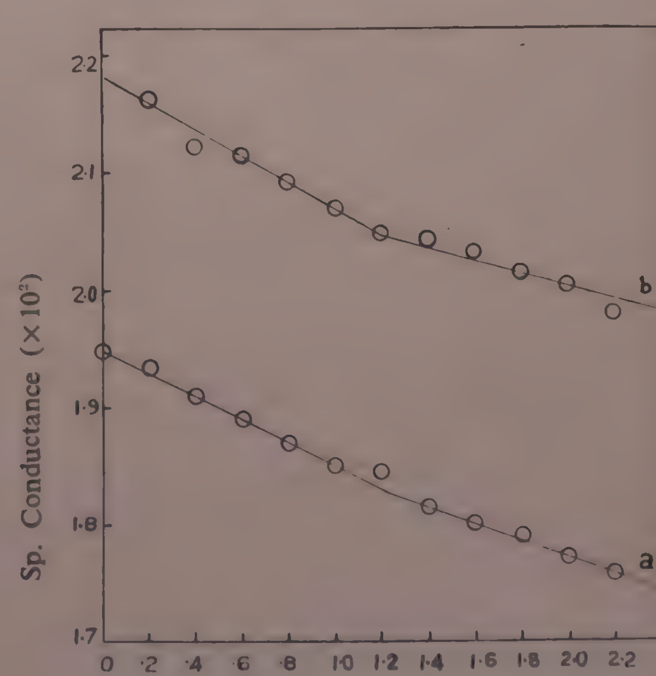
Experimental

Hexamino cobalt chloride, $[Co(NH_3)_6]Cl_3$, was prepared by the method of Biltz[6]. A concentrated solution of cobalt chloride (20 g.) and ammonium chloride (6 g.) was mixed with a solution of silver chloride in 20 per cent aqueous ammonia. The mixture was kept in a thermostat at 40°C for 24 hours while air was passed through it. The precipitate was filtered and extracted with water at 25°C. The filtrate and washing at 80°C were treated with hydrochloric acid (conc.) to precipitate the silver and the filtrate was cooled. The product was finally recrystallized from water. Analar cobalt chloride and ammonium chloride were used in the experiment.

Cobalt was estimated by the usual volumetric method and stock solution of 1.860×10^{-3} M hexamino cobalt chloride was prepared. Biuret used was of Analar variety. The pH was adjusted by 0.1N caustic soda. Conductometric titrations were made with the help of Philips conductivity bridge (PR 9403) at a constant temperature of 25 ($\pm$0.02)°C. pH. The spectrophotometric measurements were done with the help of a Russian Spectrophotometer type CΦ4 using 1.0 cm quartz cell.

Discussion

Absorption spectra of hexamino cobalt chloride alone at pH 1.6 reveal λmax at 520 mμ but that of the mixture of hexamino Cobalt Chloride and biuret (in



Vol. of Biuret (0.95×10^{-3}M) Added, ml.
Fig. 1—Conductometric Titration at pH 1.6 (2 ml. of 1.86×10^{-3}M hexamino Cobalt Chloride were taken in each case).

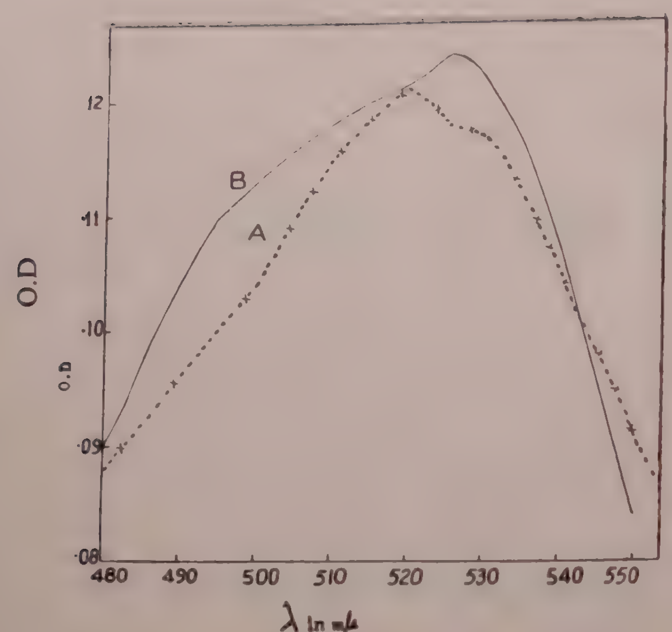
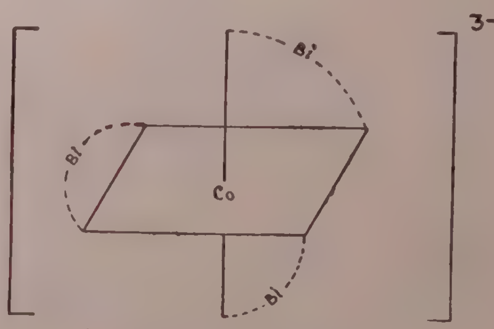


Fig. 2—Absorption Spectra at pH 1.6
A: Hexamino Cobalt Chloride
B: 1:3 Cobalt^{3+} biuret

the ratio of 1 : 3) at pH 1.6 show a shift (λmax =525 mμ). This shift in λmax gives an indication of the complex formation between cobaltic salt and biuret (Fig. 1.)

Conductometric titrations of hexamino cobalt chloride at two different specific conductivities and at the constant pH 1.6, by 0.95×10^{-2} M biuret show an appreciable break in the ratio of Co^{3+}: biuret 1 : 3 (Fig. 2).

Taking these observations into account, it may be assumed that hexamino cobalt chloride forms a complex with biuret at pH 1.6 and the structure of the complex is probably



where, Bi = Biuret

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Phosphorite Occurrence in Nainital Area, Uttar Pradesh

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A new occurrence of sedimentary rock phosphate has been reported in the Nainital region within the *Krol* limestone. Individual strata show huge variations of P_2O_5 content from 0.1 to over 30 per cent.

Although occurrence of sedimentary phosphatic rocks in India was first reported in Mussoorie as early as 1884, no systematic exploration was undertaken till recent times. This field has been put under investigation by the G.S.I. since 1961 and an extensive exploration was commissioned only in 1965-66. Phosphates of sedimentary origin provide over 85 per cent of world's P_2O_5 requirements. From this angle therefore, and also because of their resemblance to the huge north-western deposits of USA, these deposits of India deserve special attention.

Significant deposits have been located in the Barmer district of Rajasthan and Dehra dun, Pauri and Tehri-districts of Uttar Pradesh. The work carried out by the G.S.I.[1] revealed that the phosphorite formations of Mussoorie were restricted mostly to the lower *Tal* carbonaceous shales near their junction with the underlying *Krol* limestone. In absence of any physical diagnostic characteristics to locate phosphate-bearing rocks, this *Krol-Tal* contact served as a most important clue to the solution of the problem.

According to Gansser[2], in the Nainital region, a 500 m. thick quartzitic formation is covered by a section similar to the Krols. On the basis of this *Krol-Tal* association of Nainital, preliminary geological work was taken up by us in this region, whose geological set-up compares favourably with that of the Mussoorie area.

During this investigation, two exposure of phosphate bearing rocks have been located close to the Nainital lake, due west of Tallital, near the 7716 ft. peak, restricted within the upper Krol limestone. The formation, as such, is 1.5 metre thick with the individual stratum showing a wide degree of variation in the P_2O_5 content. Analysis of about sixty samples show that though the P_2O_5 content is very low (of the order of 0.1-0.9 per cent) in most strata, two 12 cm thick beds show the presence of very high amount of P_2O_5—in one, it is as high as 30 per cent while in the other 17 per cent. The phosphate-bearing beds are associated with black chert and soft shale. The entire formation is overlain by massive limestone, slightly dolomitic in nature and underlain by banded siliceous limestone. The beds dip at an angle of 35° towards North North-East, direction. The phosphorite formation can be traced along the strike direction for about 75 metres.

Infra-red studies were carried out for these samples in the solid phase by KBr-pellet technique along with those* from Kimoi in the Mussoorie region. The spectra show absolute identity of the two phosphate samples. It may be observed, however that in the Mussoorie area the phosphorite formations were restricted to the lower *Tal* carbonaceous shales along its contact with the upper *Krol*, whereas in Nainital area, it appears, the phosphorites occur within the upper *Krol* limestone. The existence of these formations in this area has not been reported earlier. Further studies are in progress to determine as to whether these are local or persistent in nature.

The authors wish to thank to Dr. K. R. Chakraborty, General Manager, P & D Division, for his encouragement and to Sri S. C. Chakravarty, Superintending Geologist, U. P. Circle, Geological Survey of India, for valuable suggestions. Thanks are also due to Sri S. K. Saxena for carrying out the chemical analyses.

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*These samples were obtained through the courtesy of Sri S. C. Chakravarty, Superintending Geologist, U. P. Circle, G.S.I.

Notes & News

New Urea Processes

A new integrated ammonia urea process has been announced by the Toyo Koatsu Industries, Inc. In this process CO_2 from the scrubbing solution, in the manufacture of urea, is compressed to the urea synthesis pressure and introduced at about 300 atm into the reactor with liquid ammonia produced in the ammonia synthesis loop. It is then pumped into the urea reactor at medium pressure, 250 atm., and 180-190°C —at which degassing occurs. Separating as crystals from the reaction mixture, the urea is prilled. CO_2 in the reformed gas is selectively absorbed under the high synthesis pressure by carbamate solution from the urea plant and liquid ammonia from the ammonia synthesis loop. Then CO_2 is directly introduced into the urea reactor. Thus the liquid mixture from the urea reactor is processed into product urea by Toyo Koatsu's process.

The features of the new process are (1) elimination of CO_2 compression, (2) simplified ammonia pumping, (3) efficient CO_2 removal, (4) improvement in thermal efficiency, (5) elimination of NH_3 regeneration from purge gas recovery system, (6) possibility of centrifugal compression for synthesis gas for lower capacity plant and (7) reduction in size and hence cost of urea reactor.

Toyo Koatsu claims that in this process (1) overall capital costs of the integrated ammonia/urea plant are reduced by 5-10% and (2) that operating costs are reduced by 6 to 7 per cent compared with the conventional process.

The product quality produced by the new process is the same as that obtained in the conventional Toyo Koatsu Process. (Nitrogen, No. 43, Sept/Oct. 1966, p. 26)

Another new process—CPI-Allied Chemical—does not involve carbamate recycle. Its technique is based on recovery and recycle of unconverted NH_3 and CO_2 as pure components. Corrosion control has been achieved by lining with zirconium the synthesis reactor, which can operate at 380 to 450°F thus permitting high conversion rates of CO_2 to urea (80-85 per cent). Developed by the Chemical Process of Ohio Inc., it has gained industrial acceptance and "total urea tonnage from plants now in production and in the engineering and construction stages is about 3000 tons/day. The new process takes only half-an-hour for full start—up from standby. The low maintenance required in the synthesis section and the gain in on-stream time are two important factors in reducing urea costs. By combining the zirconium welding techniques—which are difficult—developed by Vulcan-Cincinnati with the thermal shrink-fitting technique of Struthers Wells Corpr, a successful method has been perfected for lining the reactor's steel shell with zirconium. After urea has been separated and all carbamate has been dissociated, the products (NH_3 and CO_2) are treated with monoethanolamine solvent which absorbs selectively all CO_2 returning pure ammonia to the reactor.

The process is adaptable for once-through, partial or total recycle. Carbon dioxide, ammonia and ammonia recycle enter the reactor operated above 400°F and 4000 psi. The NH_3 to CO_2 ratio is kept between 4 : 1 and 4.5 : 1; the amount of CO_2 present as carbamate in the off-gas stream passess into the primary decomposer, which is a counter-current heat exchanger designed for high speed flow. Decomposition products (NH_4 and CO_2) and water vapour are flashed off and escape as overhead from the separator, while the urea solution passes into a small stream-heated fulling film counter-current stripper, where any ammonia is removed. At the operating conditions of the primary decomposer nearly 90 per cent of the carbamate dissociates into CO_2 and NH_3, so that the final CO_2 content in the urea stream going to the secondary decomposer is quite low—1.5 per cent of the original. The possibility of urea turning into biuret is practically nil.

The aqueous urea passes into the secondary decomposer and then to an evaporator, while the overhead streams from the primary and secondary decomposers go to the absorption unit.* The evaporator is a centrifugal, thin-film evaporation unit equipped with rotary plates and baffles and stream-jacketted on the shell side. A stripping stream of air moves counter-currently dehydrating rapidly at as low a temperature as possible to minimize biuret formation. Biuret in the prilled product is below 0.7 per cent.

[Chem. Engng., 73 (20) (1966), 96-98]

Large Tonnage Recycle Urea Plants by Chemico.

Chemico made a study on the design of a 1,500 tons/day complete recycle plant and found that a single stream plant of this capacity is entirely feasible and the economics of production will be attractive. The sizes and weights of the principal equipment items such as reactor, decomposers and carbamate condensers have been found to be normal and not unusual and only one each of these major items of equipment is required. The size of the reactor for 1,500 t.p.d. production capacity becomes fixed when the feed molar proportions and the operating temperature are established. The operating pressure is determined by choosing a practical loading density. A high conversion of carbamate to urea per pass is achieved by providing reactor intervals. The design of the reactor and its intervals is based on a knowledge of the process dynamics gained from practical experience. For minimizing the size and cost of the decomposers, it is necessary to know exactly what the overall heat transfer coefficients are. The sizes and weights of the condensers will present no problems in shipment and erection. In a urea plant, the greatest consumption of electrical power-about 65 per cent—is due to the compression of CO_2 gas and so for a production of 1,500 t.p.d. centrifugal compression should be considered. A single triplex plunger pump is sufficient to handle the recycling of carbamate solution. Chemico claims that steam and cooling-water consumption are the lowest by using a heat recovery technique and the lowest percentage of water in the carbamate recycle solution. The Chemico heat recovery technique consists of utilizing the heat of condensation of the carbamate

(gases) from the first stage of decomposition as the heat necessary to carry out the second stage decomposition. This process has been termed Thermo Urea process. This concept requires the use of external steam for carbamate decomposition, even though good heat recovery reduces steam requirements and cooling water for carbamate condensation. The heat of condensation of carbamate is recovered at a high temperature level and utilized to produce the steam required for decomposition and urea finishing. The cost of plant using thermo urea process will be less than that for a plant employing the carbamate solution recycle technique.

A modification has been made by the Chemico in the synthesis of urea for ammonia and carbon dioxide whereby unconverted reactants may be recycled to the synthesis step while avoiding the recycle of excess water. They employ a crystallization and melt system which, it is claimed, reduces biuret content. Urea is separated from feed in a vacuum crystallizer, the crystals are separated from the mother liquor in a centrifugal, dried and remelted with steam.

[Nitrogen No. 43, Sept/Oct, 1966, p. 21]

Nitrophosphate Processes: Advantages and Disadvantages

Due to shortages of sulphur in the world its price is getting increased day by day and it is becoming very expensive to manufacture most of the phosphatic fertilizers which involve the use of sulphuric acid. Nitrophosphate's production involves less or nil use of sulphuric acid. In this process rock phosphate is reacted with nitric acid. The price of nitric acid is expected to fall because of technological improvements in converting ammonia to nitric acid. This is why the fertilizer manufacturers are taking interest in nitrophosphate processes. In some of the processes calcium nitrate is removed by cooling, crystallization and centrifuging to balance the amount of calcium that is available for combining with the phosphate so that upon ammoniation no calcium phosphate more basic than dicalcium phosphate will form. The mole ratio of CaO: P_2O_5 in phosphate rock ranges from 3.3 to 4.0. Since the ratio for dicalcium phosphate is 2, at least 40 to 50% of the calcium must be removed or combined with anions other than (PO_4).

In practice, some water-soluble P_2O_5 usually is desired in the final product so that the ratio of available CaO to P_2O_5 is adjusted to less than 2; part of the P_2O_5 forms water-soluble ammonium phosphate or monocalcium phosphate upon ammoniation. If the water solubility is obtained by using increased amounts of sulphuric or phosphoric acid in the mixed acid processes, less sulphur is saved and some of economic advantage is lost.

By reaction of sulphuric acid with phosphate rock and then by ammoniation Diammonium phosphate and ammonium sulphate are produced, as separate products and as combination such as 20-10-0 and 19-19-0. They are fully water soluble and relatively nonhygroscopic. The disadvantage is the high raw material cost and relatively low analysis.

For ammonium phosphate nitrate the grades range from 30-10-0 to 25-25-0. Urea ammonium phosphate compounds are produced by several Japanese firms. N-P grades range from about 20-40-0 to 34-17-0. Both of the above fertilizers have the advantages of water solubility, high analysis and fairly good flexibility as to grades that can be made either as compounds or blends. The main disadvantage is the high sulphur requirement, about 0.94 ton of sulphur per ton of P_2O_5. For the best physical properties of triple superphosphate, it should be ammoniated or treated with basic conditioners, especially when mixed with ammonium nitrate or urea. Ammoniation reduces the P_2O_5 water solubility to a minimum of about 50 per cent. One advantage of triple superphosphate is the wide range of grades that can be made; in combination with ammonia and ammonium nitrate, grades range from 8-32-0 to 24-12-0. N-P-K grdes range from 6-24-24 to 15-15-15. No nitrogen grades may also be made. The sulphur requirement is about 0.67 ton per ton of P_2O_5 appreciably less than for ammonium phosphate. Mixtures containing triple superphosphate are somewhat lower in analysis than those made with diammonium phosphate.

Nitrophosphates made with phosphoric and nitric acids are produced commercially in several plants in the U.S.A. and Europe. Typical grades are 20-20-0, 24-12-0, 15-15-15, 10-20-20, 13-13-21 and 10-15-20. When formulated to contain 40% of their P_2O_5 in a water soluble form, the sulphur requirement 0.6 ton per ton of P_2O_5 is slightly less than for triple superphosphate. The analysis of mixtures is about the same as those made with triple superphosphate, but there is less flexibility as to grades.

In the Odda process for the reaction of phosphate rock with nitric acid and the related manufacture of an NP or NPK fertilizer, various modifications are widely used in Europe. Its outstanding advantage is that it requires no sulphur and hence the raw material costs are low. The P_2O_5 water solubility depends on the proportion of calcium nitrate removed, commercial products usually range from 35 to 50 per cent water solubility. Typical grades are similar to those made by mixed acid process with minimum N: P_2O_5 ratio 3 to 4. Calcium nitrate removed is treated with ammonia and CO_2 to convert to ammonium nitrate and calcium carbonate. In the Odda process there is relatively high investment cost and this is the disadvantage. Nitrophosphate process is an entirely water soluble product in which the phosphate may be present entirely as diammonium phosphate. The most disadvantage is the lack of flexibility as to N: P_2O_5 ratio which is about 2 : 1. The other disadvantage is that much water is introduced into the process in the sulphate cycle, all of which must be evaporated. A new process which is combination of the two preceding ones has been developed. After dissolution of phosphate rock in nitric acid, calcium nitrate is removed to whatever extent and converted to ammonium nitrate as in the Odda process. The calcium remaining in the solution is precipitated as calcium sulphate by addition of ammonium sulphate. The process has the advantage that the product has high water solubility and there is some flexibility in N:P_2O_5 ratio. The products might include ammonium phosphate nitrate ranging from 30-10-0 to 25-25-0 of several nitrophosphate processes. Modifications of the Odda and sulphate recycle processes offer the greatest potential saving because they require no sulphur, while producing fertilizers of good quality. The equipment required for the Odda process and sulphate recycle process is complex and expensive but the need for production of sulphuric and phosphoric acids is eliminated and as a result there is not much difference in investment costs.

[Travis P. Hignett, Proceedings of the 15th Annual Meeting, Fertilizer Industry Round Table, Nov. 10-12 1965 held in Washington]

To obtain nitrophosphate by treating nitric acid on phosphate rock, the main problem is the removal of undesirable calcium nitrate left in the product which causes the fertilizer to be extremely hygroscopic and too unstable to dry properly.

In the manufacture of products containing 100 per cent water-soluble P_2O_5 by the nitric acid process all of the Ca $(NO_3)_2$ i.e. CaO has to be removed. It will, of course, be more economical to remove only a portion of it so that water solubility of P_2O_5 is at least 40 to 50 per cent. If the insoluble tricalcium phosphate in phosphate rock is to be converted to soluble forms, for each mole of P_2O_5 one mole of CaO must be removed in going to citrate-soluble dicalcium phosphate, two moles in going to water-soluble monocalcium phosphate and three moles in going to water-soluble ammonium phosphate. CaO can be removed in the following ways: (*i*) by cooling, crystallization on centrifugation of calcium nitrate by Odda process. The calcium nitrate crystals can be processed to a valuable by-product; (*ii*) carbon dioxide can be used to precipitate unwanted calcium as calcium carbonate which is called carbon-nitrate process, (*iii*) by adding sulphuric along with nitric acid calcium is precipitated as calcium sulphate and the remainder is converted into dicalcium phosphate and the process is known as "Sulpho-nitrate process'; (*iv*) the digestion can be done with a mixture of phosphoric and nitric acids in the proper proportions to convert all the calcium to dicalcium phosphate. This is the conventional "Phosphorus Nitrate Process"; (*v*) the calcium nitrate can be precipitated as dicalcium phosphate with diammonium phosphate or triple superphosphate and ammonia. In this case also, calcium is discarded as calcium sulphate when producing the phosphoric acid used in making the superphosphate; (*vi*) ammonium sulphate or potassium sulphate can be used, if available, in sufficient quantity to react with the unwanted calcium to produce calcium sulphate, the remainder of the calcium reporting as dicalcium phosphate in the complex.

The mixed acid processes for nitrophosphate production have advantages of comparative simplicity, lower investment cost and flexibility. But the disadvantage is the requirement of substantial amount of sulphuric or phosphoric acid. If water solubility of 40 per cent is needed about 60 per cent as much phosphoric acid is used as in production of diammonium phosphate and only slightly less than in production of triple superphosphate.

In the latest TVA modification of the nitrophosphate process using mixed phosphoric and nitric acids, a preneutralizer is used. Phosphate rock is treated with nitric and phosphoric or nitric and sulphuric acids and the tanks employed were equipped with thorough agitation and mechanical foam breakers. The slurry flowed by gravity through the extractors and into the preneutralizer where ammonia is added. When phosphoric acid was used as the supplemental acid 70 to 85 per cent of the total ammonia wasted fed to the preneutralizer, decreasing water content of the slurry from about 26 to about 6 per cent; use of gaseous ammonia provides greater heat of reaction and results in greater evaporation of water from the slurry. The remaining 15 to 25 per cent of ammonia was fed through a drilled pipe sparger beneath the bed. When three component grades were produced, the potassium chloride was fed to the drum with cooled recycle. Single deck screens and chain mills are preferable for sizing and crusting operations. N : P_2O_5 ratios of the end-product from 1 : 2 to 2 : 1 were satisfactory and potash may be added suitably.

The advantages of this process are: to cut recycle requirement about in half, yet retaining advantages of the rotary drum ammoniator. Flexibility for production ratios for 1 : 2 to 1 : 1 system is simple.

D. S. M. Processes: In the DSM plants the following two procedures are used for the removal of the CaO. (1) Precipitation as $CaSO_4$. This is effected by adding to the decomposition liquid, a saturated $(NH_4)_2SO_4$ solution obtained as a by-product in the manufacture of caprolactam. Such an amount of $(NH_4)_2SO_4$ solution is added that all of the CaO precipitates as $CaSO_4$, which is then removed by filtration.

In this way end-products are obtained the phosphate in which is virtually 100 per cent water-soluble. The N/P ratio in these fertilizers cannot, however, be less than 1 : 6. The product having an N/P ratio=1 : 6 contains about 25 per cent N and about 15 per cent P_2O_5.

Shaping is done by granulation in a pugmill but can also be done by prilling.

(2) *Crystallization as $Ca(NO_3)_2$ 4 aq.:* Using this process, an NP fertilizer is produced the phosphate in which is 50% water-soluble. In this case, so much $Ca(NO_3)_2$ has to be removed by crystallization and subsequent centrifugation that, theoretically, the molar CaO/P_2O_5 ratio in the remaining solution is 1. (Owing to the presence of fluorine, which also binds Ca^{2+} as the insoluble CaF_2, this ratio may in practice be about 1 : 3.)

The N/P fertilizer obtained by this process contains 20 per cent N and 20 per cent P_2O_5. By incorporating potassium sulphate an NPK fertilizer containing 14 per cent N, 14 per cent P_2O_5 and 14 per cent K_2O can be made. These products are prilled in air. A great advantage of prilling as compared with other granulation techniques is that the diameter of the prills varies between very narrow limits and that the amount of off-size product is less than 5 per cent.

All the NP and NPK products produced by D.S.M. are coated with 2.5 per cent of kieselguhr.

Odda Process: The Odda process is designed for the manufacture of concentrated NP or NPK fertilizers without the use of sulphuric acid. The following are the unique features: (1) no requirements in sulphuric acid or phosphoric acid, (2) total recovery of calcium and P_2O_5 from rock phosphate in the form of dicalcium phosphate, ammonium phosphate and calcium nitrate respectively (3) NP products in the range from 15/30/0 to 25/31/0 preferably NP 20/20/0 can be produced, (4) application of NP products and calcium nitrate respectively, (5) disposal of calcium carbonate is easy. Despite the considerable flexibility in dealing with the calcium nitrate by-product, there remains the disadvantage that the process necessarily produces nearly 2 tons of fertilizer nitrogen for each ton of fertilizer P_2O_5 which is a serious disadvantage when the two elements are not needed in that ratio or where the nitrate form is not the preferred form.

The complexity of the Odda process and its relatively high investment cost are often considered to be disadvantages.

[Proc. of the 15th Annual Meeting, Fertilizer Industry Round Table, Nov. 10-12, 1965, Washington, USA]

Filtration in the Manufacture of Phosphoric Acid

In the wet process manufacture of phosphoric acid, filtration for separation of gypsum crystals is a major part involving about one third of the total cost of production in a modern plant.

During the reaction of phosphate rock with sulphuric acid, gypsum crystals must be formed that do not contain appreciable amount of P_2O_5 and that are of suitable size and configuration for separation from the acid phase in the filtration operation. Various impurities contained in rock phosphate may interfere with the formation

of crystals and a change in the source of rock can upset the crystal habit considerably. The higher strength and more viscous acid slows down filtration and has the adverse effect of decreasing crystal size (which makes filtration more difficult). Still the savings of heat in subsequent evaporation plus the smaller amount of liquor to be drawn through the filter have caused industry to raise the P_2O_5 concentration from 25 to 32% and there is an increasing trend for operation at 35 to 45 per cent P_2O_5.

In the reaction anhydrite and hemihydrate types of $CaSO_4$ are formed at higher and intermediate temperatures and concentrations respectively. Because both the anhydrite and hemihydrate crystals are stable under proper conditions, past and future processes have used and will use them to produce higher strength P_2O_5 from filtration.

Various types of gypsum crystals appear, such as rhombic, clusters, needles and plates which depend on the phosphate rock source, operating conditions and probably on the reactor design. The first two crystal types are easy to filter but the last two are very difficult.

In general, high sulphate ion concentration leads to needle-like crystals that are difficult to wash, thereby reducing P_2O_5 recovery. Intermediate sulphate ion concentration gives rhombic and cluster types of crystals. Lower sulphate ion concentrations produce small plate type crystals which are impossible to filter and wash at a satisfactory rate. Once crystals have been formed the problems in their separation include cloth binding, washing and recovery, filtrate clarity and corrosion.

At present in all large plants circular, horizontal Bird-Prayen and Eimco tilting pan filters are used. The pie-shaped pans are connected to a vacuum distributor. As the unit rotates the pans are consecutively loaded with slurry dewatered, washed and rewashed (all under vacuum) until they are finally tilted and blown with air for cake dislodging and discharging. The pans then pass through cloth cleaning and drying cycles and move from there to the feed section once again to repeat the cycle.

Large capacity per square foot of filter area requires that this type of filter be in service as much as possible. Thus, the circle units can filter during the entire cycle. The good wash provided by high pressure water (when the pans are inverted) permits the tilting pan units to stay on stream almost continuously.

Two or three counter-current washes in a modern filter have improved P_2O_5 recovery which through good displacement on the rotating pan filter is in the neighbourhood of 97 to 98 per cent. A good operation target is 10 per cent of water soluble P_2O_5.

In the filtration and crystal growth operations, the recent improvements have been: (1) in high-pressure (200 to 1,000 psi) water-cleaning of filter cloth, (2) acid dilution and cooling prior to its addition to the reactor. The heat removed by this step reduces the violence of reaction and of undesired nucleation and subsequent decrease in crystal size. (3) Increased concentration of solids in the reaction.

Processes are being developed whereby filters will have greater capacities. Some chemical industries of Japan have developed processes where nuclei are added for more uniform crystal formation.

In the U.S. Singmaster and Breyer Inc. have announced their 42 per cent acid product from the filter as compared to conventional 32 per cent strength. This they accomplish by filtering hemihydrate crystals and then redissolving them before forming gypsum.

[Chemical Engineering, **73** (17) (1966), 137]

Condensed Phosphates: Production, Properties and Fertilizer Values

Condensed phosphates contain orthophosphates and complex salts included in polyphosphates like pyrophosphoric acid, tripolyphosphoric acid and trimetaphosphoric acid.

Metaphosphates: There are two types of processes for production of metaphosphates, one based on elemental phosphorus and the other on wet-process phosphoric acid.

Tennessee Valley Authority, U.S.A. has worked out the processes for (1): burning elemental phosphorus, then reacting P_2O_5 with various products such as rock phosphate for calcium metaphosphate (CMP), a potassium salt for potassium metaphosphate (KMP), ammonia for an ammonium salt for ammonium metaphosphate (AMP).

Processes using wet-process phosphoric acid exist or are being investigated with a view to conform to the main disadvantage of the dry processes—the high energy cost neded to produce elemental phosphorus. The best known process is that of the Scottish Agricultural Industries Ltd. (SAI): its principle consists of layering a film of slurry of potassium chloride and phosphoric acid on a rolling bed of granules at about 480-500°C. A high circulating rate is achieved by using two concentric rotary drums.

Calcium Metaphosphate (CMP): CMP by the TVA process contains 63-65 per cent P_2O_5 soluble in AOAC neutral ammonium citrate. A Polish process product is almost completely soluble in 2 per cent citric acid solution and it contains more calcium. It is nearly insoluble in water and cannot be ammoniated but it can be partly hydrolyzed with hot water which makes it water-soluble and capable of absorbing ammonia. It has been possible to produce compound fertilizers with grades of 6-24-24, 11-22-11, 13-13-13, containing 20-40 per cent P_2O_5 in water-soluble form. Reaction of CMP with ammonia under pressure yields a 8-45-0 product containing 40 per cent water-soluble P_2O_5.

Potassium metaphosphate (KMP): Most KMP products which contain nearly 100 per cent nutrients, are only slightly water-soluble. The SAI product contains 5 per cent of its P_2O_5 in water-soluble form, about 50 per cent soluble in 2 per cent citric acid solution, but as much as 90 per cent when citric acid is present in excess.

Ammonium Metaphosphate (AMP): Containing 90 per cent nutrients (17% N, 73% P_2O_5) AMP consists of a mixture of 70-75 per cent ammonium metaphosphate ($(NH_4PO_3)_n$), 10-20 per cent phosphoronitridic acid (HNPOOH) and 10-15 per cent ammonium phosphoronitridate (HNPOOH NH_4). It dissolves slowly in water and is almost completely soluble in neutral ammonium nitrate.

With acid containing 70-80 per cent P_2O_5 an 11-37-0 solution with 70 per cent of its P_2O_5 in the polyphosphate form can be produced. Maximum solubility of a NP solution increases from 39 per cent in the orthophosphate system to 46 per cent at the 45 per cent polyphosphate level and to 48 per cent at the 70 per cent polyphosphate level.

Polyphosphates are excellent complexing agents of insoluble ions. The main advantages of condensed phosphates in their high nutrient content, enable fairly cheap long distance transport. By using polyphosphates it is possible to increase substantially the grade of liquid fertilizers containing phosphates. Investigations have

shown the good fertilizer value of these phosphates. However, they may be more slow-acting on crops than conventional soluble phosphate fertilizers, and it is suggested that uptake of condensed phosphates takes place after hydrolysis to orthophosphates, and this hydrolysis is mainly dependent on the biological activity of the soil. Powdered forms should be preferable to granular forms.

pH also has an influence on the effect of metaphosphates, which is lower than that of superphosphate in acid soil, but almost equivalent in neutral to alkaline soil.

Despite their agronomic value these phosphates are, as yet, hardly used. The reasons for this are: first, manufacturing processes have not yet been applied on an industrial scale; second, most of them, and in particular CMP and KMP, are insoluble or not very soluble in the conventional reagents, and so cannot be commercialized under the present legislation of many countries. Their high concentration is, however, an advantage for export markets, and it is suggested that condensed phosphates may, in future, play a part in the development of fertilizer consumption and of aggriculture in general in the developing countries.

[NPKS Abstrs, 1 (1966), Feb. 4]

Air Pollution and Dust Control in the Fertilizer Industry

To keep the air and streams clean from dust, gases and wastes of industries, suitable laws should be framed so that the industrialists are forced to use necessary equipments to control this nuisance. Most of the fertilizer plants are dusty. Good dust control will result in (1) a more uniformly granulated product free of contamination and dust,(2) better inventory control and (3) safer working conditions.

The main dust producing operations in mixed fertilizer plants are material handling devices, conveyor belts, screens, elevators and bagging stations; Ammoniator or pug mills and dryer and coolers. Control of the dust from material handling and bagging stations is relatively easy, since the dust is of rather large size and can easily be collected by dry centrifugal devices or cloth collectors. The control of dust from the ammoniator, dryer and cooler is difficult and complex. The following improvement plans were formulated by Heil Process Co. to control air pollution.

1. *Furnace Modifications:* The furnace was lengthened 3 feet to create an air chamber between the furnace and dryer so that the flame did not extend into the dryer with the possibility of decomposing fertilizer and creating fume.

2. *Product chute:* The product chute was routed through an air chamber. In addition, this chute was located behind a wall of fire bricks, out of the direct path of hot air. This also eliminated a possible source of fume.

3. *The Discharge Plenum Chamber:* A larger chamber was designed to lower the air velocity and return to the system by gravity dust which was formerly sucked out of the dryer and conveyed to the dust collectors. This reduced the load to the cyclone and scrubbers and thus the loss to the atmosphere.

4. *Cooler Plenum:* This chamber was renewed to obtain the result described above.

5. *Cyclone Air Locks:* Motor driven air locks were installed on the cyclones. These units replaced gravity operated flap gates. The results were a much better seal on the cyclone discharge and greatly increased cyclone efficiency. This also reduced the load to the scrubber and consequent loss to atmosphere.

6. *Fans:* The fan speeds were altered to restore the air flow to design conditions taking into account plant modifications.

7. *Ammoniator Scrubber:* A new medium pressure drop Venturi type scrubber was installed. This unit scrubs about 6000 cfm of air which had gone directly to atmosphere in the past. This installation most certainly reduced the fume from the stack.

8. *Ammoniator Interior:* All the interior ammoniator piping was removed and was replaced with redesigned piping in an effort to control the chemical reaction and the creation of unnecessary fume. At the same time, the bed was deepened for similar reasons. This modification included installation of a reciprocating scraper which reduced the drag and allowed us ro use the existing ammoniator drive.

9. *Dryer-Cooler Scrubber:* The dryer-cooler scrubber was modified to increase the efficiency of this unit from about 80 per cent to about 90 per cent. This represented a 50 per cent reduction of inefficiency and thus, this improvement alone cut the stack emission in half.

The conditions that make the dust difficult are temperature, moisture, corrosive materials; relatively large quantities of dust, plus, in many instances, large quantities of submission fume; and hygroscopic material. There are different types of dust collectors for different fertilizer grades. Wet collectors with medium pressure 5″ to 6″ H_2O gage have efficiency down to the 2 micron range and these will eliminate dust discharging from the cooler and driver stack. There are high pressure drop collectors also. Use of a cloth collector will collect dust and fume but its use has got some limitations. The problems of hygroscopicity and high humidity of the gas stream cause condensation on the cloth tubes and walls of the collector. The duct work and the collector must be heavily insulated to prevent this condensation.

Ventury types are most efficient of all wet collectors which can separate 99 per cent of the dust, viz. upto as small a size as $\frac{1}{2}$ micron.

[Proceedings of the 15th Annual Meeting of the Fertilizer Industry Round Table, Nov. 10-12, 1965 held in Washington, p. 39-47]

Potassium Fertilizers in India

The only source of manufacturing potassium fertilizers for which our annual requirement is about 150,000 tonnes of K_2O is from bittern. When bitterns are evaporated a mixed salt, which is a suitable raw material for potassium fertilizers, is obtained.

The three potassic fertilizers that can be obtained from mixed salt are: (1) potassium chloride along with epsom salt, (2) potassium schoenite and (3) potassium sulphate. Processes for all the three fertilizers are developed in the C.S.M.C.R.I., Bhavnagar.

Potassium schoenite, the double sulphate of potassium and magnesium (K_2SO_4. $MgSO_4$, $6H_2O$), is obtained by flotation of mixed salt. The flotation material contains potassium chloride and magnesium sulphate in the ratio as required for the formation of schoenite and on treatment with water at room temperature with constant agitation yields schoenite.

The mixed salt obtained from sea bitterns contains potassium chloride (18-20%), magnesium sulphate (30-35%) sodium chloride (15-20%) and magnesium chloride (6-8%), the percentages of potassium chloride and magnesium sulphate being in the ratio required for formation of schoenite. Sodium chloride which hinders the formation of schoenite is eliminated by the

process of flotation using ocadecylamine acetate and highly sulphonated castor oil. The floated product containing potassium chloride and magnesium sulphate on treatment with water under constant agitation yields schoneite. A pilot plant based on the above process has been set up by the CSMRI, Bhavnagar for producing schoenite.

The manufacture of potassium sulphate is based upon the two types of mixed salt available in the Rann of Kutch and envisages recovery of the entire sulphate and potassium in mixed salt in the form of potassium sulphate. For this process the requirement of the two types of mixed salt is in the ratio of 1 : 2, that is double the quantity of the kainite and carnallite type mixed salt is required as that of carnallite type of mixed salt. It is also possible to manufacture a mixture of schoenite and potassium chloride by flotation of kainite and carnallite type mixed salt and treatment with water and this mixture can be used as fertilizer.

The present potential capacity for production of potassium from the entire sea and inland bitterns as by-product of salt manufacture is only 25,000 tonnes in terms of K_2O. For all the salt works, potassium schoenite production is recommended in view of lower capital investment and simple equipment required for the process.

[Datar, D. S., *Fertilizer News*, **11**, (12) (1966), 38]

New Process Developments in U.K.

I.C.I.'s Process for NPK: In this process phosphoric acid (35-45% P_2O_5) is neutralized with ammonia to give an ammonium phosphate slurry which is introduced into a plunger type mixture/granulator, together with ammonium nitrate liquor of 95 per cent concentration, muriate of potash and recycled undersizes granules, which are added at a controlled rate. After drying, screening and cooling, the granules are coated with china clay treated with a special oil. Formulations currently in production include 10-20-20, 12-12-18, 22-11-11 and 25-9-9. The highest 1 : 1 : 1 ratio that can presently be produced with this process is 17-17-17.

SAI-R Process: Scottish Agricultural Industries Ltd., has developed production of high analysis granular fertilizers—17½-17½-17½, 16-16-21, 23-11½-11½. The principle of manufacturing process is a reactor consisting of two drums rotating concentrically one inside the other. Fertilizer granules are built up, layer upon layer like the skins of ammonia by an internal recycle process. Nitric acid, ammonia and phosphoric acid are fed into a rolling bed of recycled material and product. As they pass round the cycle the particles are coated in turn by a layer of phosphoric and nitric acids, these being neutralized by ammonia. Potash salts in the correct ratio are also added to the cycle.

The New Fison Process: Fison's Lavington Research Station developed a process for producing and handling the molten mixtures of these salts in the particular conditions necessary for fertilizer manufacture, using the anhydrous liquids to incorporate the potash by granule formation as the malt cools. The replacement of the drying stage in the conventional product manufactured by the precise dehydration in the liquid system provides products of the highest concentration, which are also extremely hard, resistant to breakdown and are reported by unusually good storage proportion. The use of anhydrous ammonium nitrate, instead of water as a solvent, provides an important benefit in giving products—which can contain fully mixed nitrate/phosphate mixtures—of utmost importance in avoiding classic deleterious storage properties of ammonium nitrate. Elimination of drying of solids avoids the diffusion processes which result in porosity and structural weakness in conventional fertilizer granules. Potassium chloride may also be easily incorporated.

[Nitrogen 42, 1966, p. 26]

Sulphuric Acid and Lime from Gypsum

The feasibility of making domestic reserves of gypsum as the source for manufacturing sulphuric acid is under investigation. Calcium sulphate reacts with gaseous reducing agent such as carbon monoxide at elevated temperature to produce sulphur dioxide and lime. Sulphur dioxide is converted into sulphuric acid by the conventional process. The decomposition of calcium sulphate into sulphur dioxide is a complicated process, and various factors such as effects of temperature, gas composition, gas flow rate and time in furnace have to be considered. Gypsum could be decomposed quite rapidly in a fluidized bed reacter while being contacted with the combustion products of natural gas and air which could be made oxidizing, reducing or neutral varying the air to gas ratio. The reduction of sulphate to sulphide during decomposition however limited the total amount of desulphurization. The formation of undesirable calcium sulphide was found to be affected by the tempe. ature of the solids, the reducing gas composition, particle retention time in the reactor etc. The determination of the optimum conditions of the reaction with a view to finding if there were one or more combinations of variables which might provide maximum sulphide and essentially complete desulphurization involved the use of statistical designs where correlating equations for variables were developed. Separate and combined effects of different reactant factors on maximization of desulphurization as well as for formation of sulphide of calcium sulphate were investigated. The data were fitted to a second degree polynomical and optimum conditions of reactions process were found out by using IBM computer. No plant is working on this technique but sufficient work has been done to establish the operating for this process.

The process for the production of sulphur dioxide and lime on a commercial scale consists in grinding gypsum to about 8 mesh and preheating to about 2000-2200° F. A fluidized bed reactor system is used. A reducing gas mixture consisting of carbon monoxide, nitrogen, sulphur dioxide and carbon dioxide in various proportions is passed through the reactor in co-current manner. The concentration of sulphur dioxide in the off-gases, is controlled at a minimum level of 6.5-7 per cent by controlling the gas flow rate. Part of the off-gas is bled for conversion to sulphuric acid and the remaining gas is recirculated. An intercooler is used for preheating the gypsum charge and cooling the bled stream off gases. Calcium oxide is discharged from the reactor system at a continuous rate. The cost comparison of sulphuric acid production from four alternate materials is as follows:

	Capital cost per ton Acid (Rs.)
Sulphur	78
Pyrites	184
Gypsum	195
Anhydrite (Cement route)	278

[Indian Chem. J., 1 (2) (1966), 31]

New Processes for Production of Sulphur Dioxide

Three new processes have been recently developed for production of sulphur dioxide.

British Titan's Process: In this process aqueous suspensions of ferrous sulphate monohydrate are produced. These suspensions may be spray-dried to produce a solid granular material which roasted in the presence of a reducing agent, for example, carbon, until it decomposes to give SO_2 and oxides of iron.

A disadvantage of production of SO_2 from spray-dried monohydrate is that the spray drying of such suspensions requires the use of a considerable amount of expensive equipment and also the supply of a considerable amount of heat for roasting. Another disadvantage is that even a fluidized bed is not well suited to roasting. These difficulties are overcome by roasting a mixture of aqueous ferrous sulphate monohydrate, a fuel and an oxygenating gas, at a temperature preferably at between 750 and 850°C. Fuels suggested are carbon, e.g. finely divided coal or coke; carbon monoxide, oil; sulphur containing material, e.g. elemental sulphur or iron pyrites in particle size 250 to 600 microns. The oxygenating agent is passed as a mixture of oxygen and inert gas. The inert gas is to fluidize or to help fluidize or to moderate the violence of the reaction. By using iron pyrites the superiority of the process is seen. The oxygenating gas used may be either cold or preheated to 350°-450°C.

The SO_2 produced in this process is suitable for use in production of sulphuric acid.

Stauffer Process: The process developed by Stauffer Chemical Co. provides for the continuous production of SO_2 by introducing sulphur and SO_3 into an agitated pool of molten sulphur and sulphuric acid of 100 to 101 per cent acidity, the sulphur and SO_3 being introduced at rates to maintain the weight ratio of H_2SO_4 to sulphur between 30 : 1 and 2 : 1 and the SO_3 being introduced below the surface of the agitated pool, which is maintained at a temperature of from 120-150°C. The weight ratio of H_2SO_4 to sulphur is preferably kept in the range of between 5 : 1 and 15 : 1. The temperature of the reaction mixture is kept slightly above the melting point of sulphur (120°C) and preferably 132-138°C.

The reactor has to be agitated to carry out the reaction in a commercially feasible manner. Since the reaction is exothermic, the reactor is provided with a water jacket for cooling.

Saint-Gobain Process: In this process pure SO_2 is manufactured based on the reaction between sulphur and Oleum. Molten sulphur in liquid form in the temperature range 125-155°C. is introduced into a reactor containing oleum maintained at about 90°C which is below the solidification point of sulphur viz 120°C, while subjecting the reaction medium to agitation. Liquid sulphur is fed into the reactor continuously, while the withdrawal from the reactor part of the oleum, rich in SO_3 is carried out discontinuously and alternately through a filter located within the reactor. Clearing of this filter can be completed by passing gaseous SO_2 through the filter in the same direction as, and subsequent to, the passage of oleum rich in SO_3 which is preferably under the pressure of gaseous SO_2. Liquid sulphur is introduced into the reactor at the top through a pipe and the SO_2 formed is withdrawn through another pipe at the top.

[Sulphur No. 65, Aug/Sept 1966, p. 33]

Hydrofluosilicic Acid as a By-product in the production of Superphosphate of Lime

In the production of superphosphate of lime by reacting sulphuric acid on rock phosphate, a valuable by-product hydrofluosilicic acid is obtained by absorption of the waste gases in water; 6 to 8 per cent solutions of hydrofluosilicic acid form the main source in the preparation of cryolite and various inorganic flourine chemicals. In aluminium industry for every ton of aluminium produced about 0.1 ton of sodium cryolite is consumed and the entire quantity is imported at present. The by-product hydrofluosilicic acid obtained may be utilized to meet the demand of cryolite.

Conditions have been established for obtaining silica-free ammonium fluoride by disilication of the hydrofluosilicic acid by passing ammonia and precipitating silica in an easily filtrable form. When the ammonium fluoride solution obtained is reacted with sodium or potassium aluminate solution under suitable conditions, the respective cryolite is precipitated out. After a suitable drying treatment the sodium cryolite is obtained. The advantage of the procedure lies in the liberation of ammonia which could be recycled for desilication in the first stage, thereby avoiding the need for the production of hydrofluoric acid for use in the preparation of cryolite.

[V. Aravamuthan, P. S. Desikan, G. Janakiraman, K. S. Srinivasan, N. Balasubramanian, G- N. Kannan and K. V. Rangaswamy. J. & Proc. Inst. of Chem. (India) 38, (6), (1966), 278]

Seminar on Preventive Maintenance

A 2-day seminar on 'Preventive Maintenance in Chemical Industries', held at Sindri under the auspices of the Sindri Unit of F.C.I. Ltd., was attended by over 130 delegates from all parts of the country. While inaugurating it, Sri R. S. Pandey, Resident Director TISCO, stressed the need for careful operation and proper maintenance of plants, which would necessarily contribute to greater and efficient production. Such maintenance is intended to prevent break-downs taking place leading to costly stoppages of work, to idle manpower, to the employment of breakdown teams and to the discount of customers. The preventive maintenance engineer is, therefore, a very important member of the productivity team, working hand-in-hand with the production planning and development division. In working out the economics of control of corrosion, which is the main enemy of any chemical industry, it is estimated that the cost of anti-corrosion measures is no less than Rs. 150 crores/year in our country. A problem of this magnitude can only be tackled by team work between the operation and the maintenance staff and through planned studies and research.

Sri A. N. Singh, Chief Inspector of Factories, Bihar, referred to India's dependence on foreign countries for capital goods and therefore the situation warranted maximum utilization of existing resources. Our means of production cannot be allowed to be jeopardized on account of negligence or for want of maintenance they cannot be allowed to remain idle for a single moment more than unavoidable. Our machinery must not remain idle for want of spares to be imported and our entire machinery of production should be geared and maintained to the highest level of productivity. There are many factors which are involved in sustaining the level of production and productivity. A country like the USA, where more than 40 per cent of its capacity for steel production was lying idle, could afford the luxury of shut-downs and breakdowns, which a poor country like ours cannot.

In all 14 papers were presented and discussed, out of which the following were communicated from this Division of FCI Ltd.: (1) 'Some Aspects of Preventive Maintenance of Boiler Tubes and Heat Exchange Pipes' by G. S. Sinha and K. C.

Banerjee, (2) 'Influence of Crystal Structure on Corrosion Failure' by C. Arvindakshan, C. V. Srinivasan and K. C. Banerjee. (3) 'Maintenance Painting in Relation to Corrosion Prevention in Fertilizer Plants' by Y. K. Varma and H. D. Sarker, and (4) 'A Stitch in Time Saves Nine' by N. Dutta.

In the first paper, G. S. Sinha and K. C. Banerjee have tested the more common types of failures for assisting those concerned with identification of the various defects, in the incipient stage, as a means to control total failures. An analysis of a large number of failures has shown that hardly 8 to 10 per cent of them are due to defective materials of construction or a defective workmanship during manufacture, while nearly 90 per cent of the defects are attributable to service conditions, such as over-heating and creep, caustic cracking, corrosion pitting, stress corrosion and thinning. A very small percentage of accident counts are due to over pressure, penetration by other metals and strain and age embrittlement. Detailed scrutiny has made it clear that the service conditions cannot be controlled to minimize accident counts below a certain minimum, principally because the controlling factors prove very expansive. Modern methods of instrumental inspection by non-destructive physical tests have brought to us enough confidence and reliability for safe operation, without recourse to restricting diversity of load conditions.

In the second paper, the authors have reported some case histories to show the importance of the effects of corrosion on crystal structure. A number of leaks were detected on high and low pressure columns, crude argon column and nitrogen exchanger in the Air Liquid plant during high pressure testing at the Trombay Unit of FCI. The following were some of the samples: cut-pieces from weldmets, parent metals, materials adjacent to the weld and solid deposits from inside of the high pressure column of the sieve plate, etc. X-ray diffraction and thermomagnetic analyses showed austenite phase in all samples. In addition, all the x-ray diffraction patterns revealed varying degrees of lattice strain on the structure. The electron microscopic examination of the same samples revealed that in regions closer to welds there was increased density of precipitation along austenitic grain boundaries. Occurrence of crystalline precipitation of submicron dimension was also noticed.

In another case study, viz. on a mild steel water cooler in the CO_2 scrubbing section of ammonia plant of Rourkela fertilizer factory, the crackings were mainly on the welded portions of the shells and headers and also on the tube sizes which were in contact with the regenerated liquor. These crackings were more in number on the warmer portions of the shells and headers and also on the tube sides which were in contact with the regenerated liquor. Such crackings were more in number on the warmer portions of the coolers. X-ray diffraction patterns showed ferritic and pearlitic structures in all samples, while x-ray and microscopic analyses of the corrosion products revealed iron oxides, sulphides and ferrocyanides. These findings have established that corrosion of mild steel coolers by regenerated liquor was due to the interaction of dissolved chemical impurities like H_2S and HCN.

The blistering and deterioration in the inside wall of the water scrubber in the ammonia plant at Sindri, when studied under electron microscope, were found to be due to carbide precipitation and formation of ferritic boundaries resulting in intragranular cracking. H_2S present in carbon dioxide gets ionized in presence of water liberating H^+ ions. In fact alpha-structure in steels shows a characteristic embrittlement by an aqueous solution of H_2S. To prevent methane formation the carbon has to be combined with chromium, vanadium, nickel or niobium which form stable carbides.

The failure of carbon brush holders—made of brass—for the exciters of the synchronous motors in the gas reformation plant at Sindri has been found to be due to the combined influence of applied stress and exposure to atmosphere containing ammonia. The 'season cracking' in brasses can be prevented by a stress-relief anneal at about 275°C or by changing the material of construction to more resistant alloys like red brass.

In the third paper, Y. K. Varma and H. D. Sarkar have focussed on the practical problem of repainting in a running plant, structurals, etc. emphasizing the hazards encountered. They have suggested for surface preparation and maintenance painting.

N. Dutta has explained the importance of the operating staff for preventive maintenance. He has given some typical schedules for the maintenance of turbines, such as for maintenance of records of equipment, periodical overhaul and inspection for all equipment and trouble-shooting.

The reading of papers was followed up by an interesting discussion. Among many others, the following were a few salient recommendations: the use of carbon tetrachloride as a cleaning agent and wearing of synthetic fibre apparel should be forbidden, and near the gas pipes carrying inflammable gases there should be no lighting circuit or installation.

We regret to record the demise of Sri S. M. Wasi, Public Relations Adviser of the FCI Ltd., on October 28, while travelling by car from Nangal to Chandigarh. He had joined the Sindri fertilizer factory in 1951 as P.R.O. and was the Editor of Sindri News. He left Sindri in 1958 and joined in 1961 as P.R.A. soon after the formation of the Fertilizer Corporation. He was the Chief Editor of FCI News and FCI Samachar (Hindi).

Before joining FCI, Sri Wasi was a journalist working with the Associated Press of India (now PTI) and later a Liaison Officer of the National Coal Development Corporation, New Delhi.

News in Brief

TVA's Ammonium Polyphosphate

TVA has recently developed a high analysis ammonium fertilizer about 15-60-0 grade—produced by ammoniating electric furnace . superphosphoric acid under moderate pressure at about 400°F. It is granulated by a pugmill. No drying is required; production rate is about 59 tons per hour. Ammonium polyphosphate can be applied direct to soils as a solid fertilizer, or it can be blended with other materials to make various grades. Also it is suitable as an intermediate for making liquid fertilizers.

[Nitrogen No. 43, Sept/Oct., 1966, p. 42]

Effect of Heat on Ammonium Nitrate

Effect of heat on ammonium nitrate in its caking problem was studied by the Solar Nitrogen Chemicals Co. Straight ammonium nitrate and blends using varying amounts of ammonium nitrate with ammonium phosphate were tested by changing the temperature from 70°to 110°F and then back to 70°F; and this revealed considerable breakdown of the prills and expansion of individual prills, both factors contributing to caking. There are undoubtedly a number of other factors which could affect the degree of setting in addition to cycling through the critical heat point of 90°F, such as prill density, moisture content, and diluents or contaminants in the ammonium nitrate as well as types of conditioners. It is pointed out also that the amount of heat absorbed and its transfer to the ammonium nitrate vary with the type of container, the amount of insulation, the colour of the car, the size of the prill which might determine the amount of air space and rate of heat transfer; and the amount of conditioner which might act as insulation.

Thecontainers may be insulated with polyurethane type of paint which expands after application and gives as good insulation effect. On investigation it was found that more caking occurred whenammonium nitrate was hot and loaded into the container.

[Nitrogen, No. 43 Sept/Oct. 1966, p. 41]

Safety of Ammonium Nitrate

The explosion hazards of ammonium nitrate were studied extensively by the U.S. Bureau of Mines in co-operation with the U.S. Manufacturing Chemists Association. The chances of fertilizer grade ammonia to be detonated by fire under normal conditions of transport and storage are very small but cannot be ruled out completely. Nevertheless, a direct deflagration to detonation transition would appear to be possible, if at all, only in a pile of extremely large dimensions with the ignition at the bottom or centre of the pile. No transition to detonation was observed in any of the experiments in which ammonium nitrate alone was bruned. Such a transition has been observed, however, in experiments in which the ammonium nitrate was thoroughly mixed with combustible materials and continued in containers that permitted rapid build-up of high pressures from the gases generated in burning. The materials mixed with ammonium nitrate in these experiments included polyethylene, paper and fuel oil. Other tests showed that ammonium nitrate, particularly when it is hot can be detonated by projectiles propelled into it by the force of nearby explosions.

[Nitrogen No. 43, Sept/Oct. 1966, p. 41]

Half the World's Ammonia is Based on Natural Gas

Natural gas reserves discovered in the North Sea are capable of supporting production of 5000 cu.ft/day for at least 20 years and the gas would have a profound influence on the economic prosperity of Great Britain. At present half of world ammonia capacity of 18 million tons/year is produced from natural gas. By 1975 nearly 75% of world production would be so based.

[Chemical Age, **96** (2469) (1966), 828]

Nitrogen as Key Nutrient for Grasses

The key nutrient in turf fertilization according to P. E. Ricke, Asst. Professor of Soil Science, Michigan State University, is nitrogen; phosphorus and potassium etc. are usually needed in lesser quantities. A 4-1-2 ratio fertilizer, such as 20-5-10, meets the general turf fertility requirements as it is high in nitrogen. Ricke also lists 3-1-2, 3-1-1 and 4-1-1 as popular turf fertilizer ratios. Soluble nitrogen fertilizers result in higher average turf quality. A continued programme of soluble and ureaform nitrogen gives high quality turf as well.

[NPKS Abstracts, **12** (1966), July, 6]

Gypsum Mines at Jodhpur

The Jodhpur organization of F.C.I., which is engaged in the task of maintaining a continuous flow of gypsum at the rate of 2000 tons/day to the Sindri fertilizer factory, has opened two new mines—Kaoni and Bharu—in Bikaner. *Nal*, till recently an unknown place near Bikaner, has been converted into a DK station and gypsum traffic has started moving. The new mines are at a distance of 14 miles from *Nal*, the nearest railhead, to which gypsum raised is transported by road.

The mineral produced at the new mines is expected to be costing 30-40 per cent less as compared to similar mines owned by private firms. The organization is now running 12 gypsum quarries as compared to only 3 mines in 1963.

[Sindri News, **2** (4) (1966), 5]

Asphalt Helps Crop Production

Two U. S. scientists, Clarence M. Hausen and A. Earl Erickson, have developed a method that will pave the way to improve food crop production by putting a thin layer of asphalt 2 ft under a sandy soil. The layer, about one-eighth of an inch thick, provides a sort of artificial "hardpan" which doubles the soils' water-holding capacity, thus increasing yields of some crops by over 100 per cent. In 1965, the scientists saw sand soil with an asphalt layer produce 50 per cent higher potato yields than irrigated plots with no asphalt. Besides the extra profit from higher yields, there was a considerable saving in irrigation cost. Using this technique the yields

of beans and cucumbers have also been increased.

[Science & Engineering, **19** (12) (1966), 182]

Reduction of Nitrogen Losses Under Irrigation by Coating Fertilizer Granules

In greenhouse studies by the U.S. Department of Agriculture with resin-coated ammonium nitrate fertilizer applied on irrigated soils with free drainage at rates of 150, 300, 600 and 1200 mg. N per pot was found more efficient than non-coated ammonium nitrate in increasing forage yield and N content of blue panic-grass. Coating the fertilizer granules did not affect cabbage yields in field conditions. By increasing the coating thickness, however nitrogen content in cabbage is significantly reduced. N uptake and cabbage yields fell significantly as soil moisture availability declined. Soil NO_3 and mineralizable N levels indicated that the resinous membrane, by controlling fertilizer dissolution, reduced N leaching losses.

[Nitrogen No. 42, 1966, p. 45]

SlowRelase Fertilizers

Mckog-Albatros Co. of Netherlands reports that fertilizer granules with a coherent or non-coherent coating containing both a paraffin wax and a polyalkylene having a molecular weight of not more than 10,000, produced a slow-release fertilizer action. The fertilizer component may be phosphate fertilizer, potassium fertilizer, nitrogen-containing fertilizer and compound NP or NPK fertilizers. Compound fertilizers comprising ammonium nitrate, or urea as also a mixture of ammonium nitrate and calcium carbonate have been investigated.

The paraffin wax/polyalkylene mixture is liquefied by heating and sprayed on the granules, using a rotating drum if desired; or the fertilizer granules can be immersed in the melt when more than one coating is applied. The first coating is applied to warm granules having a temperature of 30-60°C so that the coating mixture can flow as smoothly as possible. Not more than 20% of the weight of the uncoated granules and preferably 10-18% is applied.

To prevent granules sticking after coating a powdering agent can be used, e.g. lime and synthetic and nonsynthetic clay materials. Increasing the polyalkylene content of the coating mixture will also prevent sticking of the granules.

[Nitrogen No. 42, 1966 p. 45]

Nickel Stainless Steel for the Largest Nitric Acid Absorption Towers

Four giant absorption towers, claimed to be the largest of their type yet built in W. Europe, have recently been fabricated entirely from chromium—nickel stainless steel with approximately 17-19% chromium and 9-13% nickel, stabilized with niobium, by Koerver and Lersch of W. Germany.

Each tower weighs 50 tons and the other dimensions are: height, 35.5 metres; diameter 4.5 metres; wall thickness of shell 8.9 and 11 mm.; thickness of tube plates, 14 and 15 mm. Design pressure is 4 kg/cm_2, with temperatures in the range of 50-100°C.

[Nitrogen No. 42, 1966, p. 46]

New Fertilizer Retards Ammonia Loss.

Toyo Koatsu Co. reports that a new product 2-amino-4-chloro-6-methyl pyridine, used with nitrogenous fertilizers, such as ammonium sulphate or urea, will check the loss of ammonia. The company claims also that in field tests, the new fertilizer increased crop yields by 3 to 5% and was particularly effective in rice cultivation.

[Nitrogen No. 42, 1966, p. 46]

Potash from Mica Wastes

Mica waste, which is available in plenty in India, contains about 9 per cent potash. A simple process has been developed for the recovery of about 90 per cent potash as soluble potassium salt using mica waste from Andhra Pradesh containing about 11 per cent potash.

Mica waste is heated with calcium sulphate or ammonium chloride, potassic sulphate and potassium chloride are respectively formed more or less quantitatively. These can be used as manures as such or crude potassium sulphate and muriate of potash can be extracted with water from the heated mass and used as manures.

[Science & Engng., **19** (1966), Nov., 164]

World Fertilizer Federation

At a meeting of FAO, on a proposal by a Dutch representative, a world fertilizer producers cooperative body has come into being. The Federation consists of an elected 9-member executive committee which is to lay down the rules by Feb. 1967. It will be formally inaugurated in July 1967. The committee consists of 2 members each from phosphate and potassium fertilizer producers; one each from sulphur producers; 3 members from nitrogenous fertilizer producers represented by the U.S.A., European countries and Japan. India represents the fertilizer consumers.

[Chem. Age of India, **17** (1966), 9, 673]

Phosphate and Soil Hardness

Water-soluble phosphate fertilizers have been shown to reduce hardness of soils. A greater reduction in hardness was obtained with soils containing 2 : 1 lattice clays than with soils containing 1 : 1 lattice clays. Phosphoric acid and superphosphate were both used on the three test soils, the former tended to reduce hardness more.

[Lutz. J. F. and Pinto, R. A., Proc. Soil Sci. Soc. Amer., 1965, 29, 458; NPKS Abstract, **1** (1966), 5]

Aqueous Fertilizer Suspensions

NH_3 is oxidized to provide a gaseous stream containing a mixture of N oxides and brought into contact with an aqueous slurry of a Ca-containing compound selected from phosphate rock and/or limestone and/or dolomite (wt. ratio water Ca compound 0.5-3 : 1) so that the slurry is acidulated to form the aqueous fertilizer suspension, part of which is cooled (to 80-200°F) and for further contact with the oxide gas stream.

[NPKS Abstrs, **1** (1966), 8]

Urea Application on Jute

The Indian Jute Industries' Research Association, which provides extension service on intensive cultivation methods, has during the current season about 2000 acres of land in compact blocks (average 150 acres each) for demonstration of intensive cultivation spread over 15 jute and mesta growing districts in W. Bengal, Bihar, Orissa, Assam and Andhra Pradesh. This service has pioneered large scale foliar application of urea on jute by the spray method which has proved to be highly economical in fertilizer consumption.

[Newsletter (IJIRA), 1 (1966), 2, 4-5]

Potassium Schoenite Fertilizer Plants

The Central Salt & Marine Chemicals Research Institute, Bhavnagar has entered into an agreement with Messrs Industrial Consulting Bureau Ltd., Bombay for designing and setting up potassium schoenite fertilizer plants on premium and

royalty basis in India and abroad, based on the process developed in the Institute. Potassium schoenite can favourably substitute potassium sulphate, which is at present entirely imported. M/s I.C.B. has undertaken at least one commercial plant each year, and the entire equipment required is indigenous.

[Salt Research & Indus., 3 (1966), 184]

Low-pressure Urea based Melamine Process Developed by Chemico

An improved, low pressure melamine process from urea has been developed by the Chemico, New York. The manufacturing cost has been reduced from 26 to 10 cents per lb by adopting this new process and the initial capital investment is also low.

The process has been experimented in a pilot-plant. Fertilizer grade urea is fed to a urea vaporizer where it is vaporized at moderate temperature and a slight pressure. Gaseous ammonia produced in subsequent processing steps is passed through the vaporizer with the urea. The vaporized stream is then fed into the converter where the catalytic conversion to melamine takes place. Melamine in the gas phase is condensed and brought into aqueous suspension in a specially designed condenser. The aqueous suspension of melamine is separated from the off-gas and then sent to a centrifuge, where the product is separated from its mother liquor. It is then washed and dried. Gas leaving the melamine separater is scrubbed in an absorber yielding a carbamate solution for recycle to the urea plant; the excess ammonia gas is then raised slightly in pressure for recycle to the first part of the melamine process.

[Nitrogen No. 42, 1966, p. 29]

CORRIGENDA

1. On page 143, Fig. 4, Technology 3(3) (1966) of the paper "Investigation into the use of Algae for removing Ammonium Nitrogen from Nitrogenous Industrial Wastes, Part 1—Laboratory Batch Studies" along the right hand ordinate Ammonium Nitrogen should be read.
2. On page 178 this issue Fig. 1 of the paper "Selective Extraction of Potassium from Sea Water, Bitterns and Mixed Salt" the intervals along the ordinate should be read as 0, 1 and 2 instead of 1, 2 and 3 respectively.

TABLE 1—WET PROCESSES FOR THE MANUFACTURE OF COMPOUND FERTILIZERS. (NITROPHOSPHATES)

Classification of Fertilizers according to plant nutrient content	Process Description	Raw materials fixed in the fertilizer: Reaction	Raw materials fixed in the fertilizer: Ammonia-tion	Raw materials fixed in the fertilizer: as CaSO aq + Cax (mol)	Raw materials fixed in the fertilizer: as $CaCO_3$ + Cax (mol)	Ca ions separated from the fertilizer slurry as as $Ca(NO_3)_2$ $4H_2O$ (mol)	previously during H_3PO_4 production as CaSO-. aq (mol)	Nutrient ratio: N/P_2O_5 % (wt)	Nutrient ratio: $N/P_2O_5/K_2O$ % (wt)	Finished fertilizer Ca compounds: $CaSO_4$ + Cax (mol)	Finished fertilizer Ca compounds: $CaCO_3$ + Cax (mol)	Finished fertilizer Ca compounds: $CaHPO_4$ CaO (part) (mol)	Finished fertilizer Ca compounds: P_2O_5 (part) (mol)	Ammo-nium phosphate P_2O_5 part	CaO/P_2O_5 Molar ratio linked to phosphate CaO / total P_2O_5	total CaO / total P_2O_5
Low-grade	(*a*) Carbon dioxide nitric acid process with phosphate rock	RP HNO_3	NH_3 CO_2	—	2.0	—	—	16.6/14.1	13/11/13	—	2.0	2.0	1.0	—	2.0 : 1	4.0 : 1
	(*b*) Sulphuric acid nitric acid process with phosphate rock	RP H_2SO_4 HNO_3	NH-	2.7	—	—	—	13.5/13.5	11/11/11	2.7	—	1.3	0.65	0.35	1.3 : 1	4.0 : 1
Medium-grade	(*c*) Sulphuric acid nitric acid phosphoric acid process with phosphate rock	RP H_2SO_4 HNO_3 H_3PO_4	NH_3	1.7 1.3 0.7	—	—	1.0 1.4 2.0	15.0/15.0 16.6/16.6 18.3/18.3	12/12/12 13/13/13 14/14/14	1.7 1.3 0.7	— — —	1.3 1.3 1.3	0.65 0.65 0.65	0.35 0.35 0.35	1.3 : 1 1.3 : 1 1.3 : 1	3.0 : 1 2.6 : 1 2.0 : 1
High-grade	(*d*) Nitric acid process with phosphate rock e.g. Odda process e.g. Kampka-Nitro process	RP HNO_3	NH_3	0.2	—	2.5	—	20.0/20.0	15/15/15	0.2	—	1.3	0.65	0.35	1.3 : 1	1.5 : 1
	(*e*) Nitric acid phosphoric acid process with phosphate rock	RP HNO_3 H_3PO_4	NH_3	0.2 0.1 0.1	—	—	2.5 3.2 3.6	20.0/20.0 21.8/21.8 23.5/23.5	15/15/15 16/16/16 17/17/17	0.2 0.1 0.1	— — —	1.3 0.7 0.4	0.65 0.35 0.20	0.35 0.65 0.80	1.3 : 1 0.7 : 1 0.4 : 1	1.5 : 1 0.8 : 1 0.5 : 1
Highest-grade	(*f*) Nitric acid phosphoric acid process without phosphate rock	HNO_3 H_3PO_4	NH_3	0	—	—	—	24.7/24.7	17.5/17.5/ 17.5	0.1	—	0	0	1.00	0 : 1	0.1 : 1

RP = rock phosphate

[The Manufacture of Compound Fertilizers By The Kampa-Nitro Process by Dr. W. H. Nees and Dr. F. W. Brandt, Proceedings of the 15th Annual Meeting Fertilizer Industry Round Table, November 10-12, 1965 held in Washington p. 83].

TABLE 2—Raw Material Requirements and Products for Selected Nitrophosphate and Conventional Processes

Product	Grade	Tons/day	Basic raw material requirement, tons/day Phosphate rock[a]	Sulphur	Ammonia	$/day	Cost of raw materials[b] $/ton of $N+P_2O_5$
DAP and AS	18-46-0 21.0-0	217 768	334	228	251	24,715	82.40
DAP and AN or urea	18-46-0 33.5-0-0 45-0-0	217 480 (358)	334	94	261	18,375	61.20
TSP and AN or urea	0-46-0 33.5-0-0 45-0-0	217 598 (446)	327	67	261	17,360	57.90
Mixed acid nitrophos and AN	20-20-0 33.5-0-0	500 299	325	60	259	17,005	56.70
Modified Odda process	20-20-0 33.5-0-0	500 299	313	0	260	14,830	49.40
Modified Odda process with sulphate cycle	25-25-0 33.5-0-0	400 299	313	0	260	14,830	49.40
Sulfate-cycle nitrophos	28-14-0	715	313	0	260	14,830	49.40

[a] 33% P_2O_5
[b] Assumed cost per ton: phosphate rock, $ 10; sulfur, $ 35; ammonia, $ 45.

[Nitrophosphate Processes—Advantages and Disadvantages by Travis P. Hignett, Proceedings of the 15th Annual Meeting, Fertilizer Industry Round Table' November 10-12, 1965 held in Washington, p. 95]

TABLE 3—World Nitrogen Production and Consumption

(in thousands of tonnes)

Summary	1960-61 Prod.	1960-61 Cons.	1961-62 Prod.	1961-62 Cons.	1962-63 Prod.	1962-63 Cons.	1963-64 Prod.	1963-64 Cons.	1964-65 Prod.	1964-65 Cons.	1965-66 Prod.	1965-66 Cons.
West Europe	5,037	3,872	5,267	4,195	5,580	4,701	6,230	5,033	6,749	5,436	7,306	5,858
East Europe	2,001	2,019	2,218	2,165	2,548	2,515	3,036	3,103	3,581	3,779	4,455	4,542
North America	4,091	3,862	4,416	4,262	4,989	4,835	5,428	5,403	6,304	6,104	6,920	6,715
Central America	35	235	59	270	124	294	194	407	224	471	291	525
South America	173	160	204	159	213	200	264	229	282	275	290	311
Asia	2,062	2,599	2,054	2,621	2,373	3,004	2,765	3,308	3,057	3,619	3,478	4,119
Africa	135	388	196	417	231	435	234	537	283	607	320	650
Australasia	24	37	25	52	23	53	23	88	31	89	35	97
World Total	13,558	13,172	14,439	14,141	16,081	16,037	18,174	18,108	20,511	20,380	23,095	22,817

[Nitrogen No. 42, 1966, p. 18]

TABLE 4—World Nitrogen Imports and Exports

(in thousands of tonnes)

	1960-61		1961-62		1962-63		1963-64		1964-65	
	Imports	Exports	Imports	Exports	Imports	Exports	Imports	Exports	Imports	Exports
West Europe	723	1,704	724	1,867	879	1,896	894	1,966	888	2,145
East Europe	207	189	203	256	246	279	346	289	378	180
North America	367	510	433	526	429	497	497	525	449	639
Central America	204	20	234	26	222	26	239	39	313	62
South America	123	135	108	144	118	134	134	169	147	158
Africa	254	1	222	4	206	2	312	9	333	9
Asia	984	313	1,017	416	1,175	529	1,168	619	1,192	641
Australasia	16	3	27	—	30	—	63	—	56	—

[Nitrogen, No. 42 July/August, 1966 p. 18]

TABLE 5—Production & Consumption of Urea in India

Year	Production, m. tonnes	Consumption m. tonnes
1956-57	—	7,189
1957-58	—	30,493
1958-59	—	63,343
1959-60	3,839	113,811
1960-61	11,765	44,494
1961-62	13,535	165,017
1962-63	18,698	184,630
1963-64	18,911	247,445
1964-65	18,144	268,087
1965-66	52,000*	345,253
1966-67	150,000*	—
1967-68	350,000*	—
1968-69	700,000*	—
1969-70	1600,000*	—
1970-71	2500,000*	

*Estimated.

[JUC News, July 1966, p. 2]

TABLE 6—Production of Different Nitrogenous Fertilizers by the End of Fourth Plan (Tentative)

[Total Nitrogen Production Envisaged—2.2 m. tonnes]

	Per cent
Urea	51
Compound Fertilizer	30
Calcium Ammonium Nitrate	9
Ammonium Sulphate & Others	10

[JUC News, June 1966, p. 1]

Table 7—Permissible Limit for Biuret Content in Urea, %

(In accordance with Fertilizer Control Order)

Country	Urea		Compound Fertilizer containing Urea	
	Biuret	Biuret-N	Biuret	Biruet-N
India	1.50	0.61	—	—
Japan	2.45	1.00	0.98	0.40

[JUC News, Oct. 1966, p. 4]

TABLE 8—STATEMENT SHOWING THE MODEL BREAK-UP OF THE DISTRIBUTION MARGIN FOR SOME FERTILIZERS IN INDIA

(Rs. per tonne)

Item of expenditure	Sulphate of ammonia	Urea	Calcium ammonium nitrate	Ammonium phosphate (20-20)	Di-ammonium phosphate (18-46)
1. Commission to dealers:					
(i) Wholesaler	3.50	6.00	3.10	5.80	7.50
(ii) Retailer	8.70	15.00	7.80	14.40	18.75
2. Incentive Commission (to be funded)	2.00	2.00	2.00	2.00	2.00
3. Administration charges	1.00	1.00	1.00	1.00	1.00
4. Transport charges:					
(i) Railway to wholesale godown	2.00	2.00	2.00	2.00	2.00
(ii) Wholesale to retail godown	8.00	8.00	8.00	8.00	8.00
5. Loading & Unloading:					
(i) Wholesaler	2.50	2.50	2.50	2.50	2.50
(ii) Retailer	2.50	2.50	2.50	2.50	2.50
6. Godown rent for wholesaler and retailer @ Rs. 0.80 p. per tonne per month for 6 months	4.80	4.80	4.80	4.80	4.80
7. Shortage for wholesaler & retailer	1.50	3.00	1.40	2.80	3.75
8. Interest charges* (4 months on an average)	9.30	16.00	8.30	15.50	20.00
9. Supervision, publicity, etc. (Apex Society of wholesaler)	3.00	5.70	3.00	5.80	5.00
10. Miscellaneous expenses	1.20	1.50	3.60	2.90	2.20
Total:	50.00	70.00	50.00	70.00	80.00

*The Committee calculated interest charges @ 8 per cent.

[Fertilizer News, **II** (12) (1966), 30]

TABLE 9—PRICES OF FERTILISERS (N, P_2O_5, K_2O) IN DIFFERENT COUNTRIES IN RELATION TO THE PRICES OF WHEAT AND RICE

Country	Kg. of wheat required to buy one kg. of nutrient						Kg. of rice required to buy one kg. of nutrient					
	1963-64 prices			1964-65 prices			1963-64 prices			1964-65 prices		
	N	P_2O_5	K_2O	N	P_2O_5	K_2O	N	P_2O_5	K_2O	N	P_2O_5	K_2O
Australia	4.2	1.1	1.6	4.9	1.3	1.9	—	—	—	—	—	—
Belgium	2.3	1.7	—	2.8	1.7	—	—	—	—	—	—	—
Canada	6.4	4.6	2.1	5.4	3.9	1.9	—	—	—	—	—	—
France	2.7	1.6	0.7	2.5	1.2	0.7	—	—	—	—	—	—
Germany (Fed. Rep.)	2.7	2.1	0.7	2.6	1.9	0.7	—	—	—	—	—	—
Italy	2.3	1.5	0.9	2.3	1.6	1.0	2.5	1.7	1.0	2.4	1.6	1.0
Japan	2.4	1.9	0.8	2.1	2.0	0.8	1.1	0.9	0.4	0.9	0.9	0.4
Netherlands	2.6	1.9	0.9	3.0	2.3	1.0	—	—	—	—	—	—
Pakistan	1.7	1.7	0.6	1.8	1.3	0.6	0.9	0.9	0.3	1.2	0.8	0.4
Taiwan (China)	—	—	—	—	—	—	3.2	1.7	0.9	3.0	1.6	0.9
U.A.R.	5.4	2.9	1.5	5.1	2.8	1.5	4.6	2.5	1.3	7.1	3.9	2.0
U.K.	2.6	2.2	1.8	2.3	1.8	1.6	0.9	0.7	0.6	0.9	0.7	0.6
U.S.A.	4.0	3.3	1.5	5.6	4.5	2.0	1.4	1.2	0.5	1.4	1.2	0.5
India	3.7	3.2	1.3	3.0	2.5	1.1	3.8	2.4	1.0	3.1	2.6	1.1

Note: Prices considered are those of ammonium sulphate, superphosphate and muriate of potash.

Statement compiled from F.A.O. Year Book.

[Fertilizer News, II (12) (1966), 12]

TABLE 10—CONSUMPTION OF N, P_2O_5 AND K_2O—STATEWISE 1965-66*

(metric tonnes)

State	N	P_2O_5	K_2O
Andhra Pradesh	78,792	30,685	2,695
Assam	5,090	2,398	343
Bihar	31,893	3,421	1,352
Gujarat	30,325	12,242	2,369
Jammu & Kashmir	3,472	127	**
Kerala	8,245	4,369	21,401
Madhya Pradesh	18,404	8,845	2,526
Madras	70,756	17,122	18,178
Maharashtra	54,124	14,266	11,662
Mysore	30,925	10,132	7,555
Orissa	15,973	1,137	963
Punjab	46,257	3,288	1,210
Rajasthan	9,042	1,241	1,108
Uttar Pradesh	88,105	5,069	4,938
West Bengal	32,388	7,488	8,440
Delhi	638	192	16
Himachal Pradesh	1,759	318	17**
Manipur	562	200	—
Tripura	250	10	—
Nagaland	12	10	—
Pondicherry	642	78	—
Goa	1,023	71	—
Dadra & Nagar Haveli	—	3	—
Andaman & Nicobar	15	—	—
Coffee Board	10,826	—	—
U.P.A.S.I.	10,277	—	—
Rubber Board	2,080	—	—
Tea (N.E. India)	22,113	—	—
Food Corporation of India	749	—	—
Used in Mixtures	—	8,323[1]	—
Industrial Users	3,852	—	906
Miscellaneous	10	6	—
India Total:	578,599	131,041	89,179[2]
Nepal	429	32	—
Grand Total:	579,028	131,073	89,179[2]

*These figures are on July/June basis.

**These are combined figures for Jammu & Kashmir and Himachal Pradesh.

Note: Calculated on the basis of distribution figures.

[1] Represents the quantity utilised by superphosphate manufactures only.

[2] Includes 7000 metric tonnes of sulphate of potash as K_2O statewise distribution figures for which are not available.

[FAI Inform. Serv., 7 (21) (1966), 7]

TABLE 11—DISTRIBUTION OF NITROGENOUS FERTILIZERS DURING 1965-66 (APRIL-MARCH)

(metric tonnes)

Distributed to*	Ammonium Sulphate[1]	Urea[1]	Ammonium sulphate nitrate[1]	Calcium ammonium nitrate[1]	Chilean natural nitrate of soda[2]	Ammonium chloride[1,3]
Andhra Pradesh	126,706	75,700	8,920	4,942	750	2,943
Assam	11,749	472	—	1,713	—	—
Bihar	68,459	13,639	4,290	10,049	—	1,320
Gujarat	88,216	17,327	2,065	3,470	280	8,280
Jammu & Kashmir	8,214	42	—	2,480	—	—
Kerala	8,824	6,256	27	7,579	477	—
Madhya Pradesh	53,386	15,898	3,840	15,392	—	—
Madras	140,252	68,793	8,684	14,171	160	1,608
Maharashtra	130,820	35,518	2,890	14,594	3,178	2,889
Mysore	74,449	21,849	—	21,298	1,059	746
Orissa	10,535	403	—	48,304	—	—
Punjab	59,129	1,312	—	203,616	—	—
Rajasthan	18,019	2,121	515	18,372	—	—
Uttar Pradesh	198,791	20,067	14,066	121,292	—	3,972
West Bengal	100,842	13,508	—	3,710	538	749
Delhi	822	44	—	2,338	—	—
Himachal Pradesh	389	44	—	9,370	—	—
Manipur	—	750	—	800	—	—
Tripura	—	—	—	1,006	—	—
Goa	3,000	372	—	—	—	—
Pondicherry	2,136	296	40	—	—	—
Andamans	3	1	—	1	—	—
Nagaland	60	—	—	—	—	—
Coffee Board	15,312	2,260	6,634	8,585	—	—
U.P.A.S.I.	45,290	1,519	—	200	—	—
Rubber Board	6,234	71	299	—	—	—
Tea (N. E. India)	93,134	796	—	—	—	—
Industrial Users	8,489	2,894	—	—	—	3,542
Food Corporation of India	—	—	—	—	—	—
Others	—	—	—	—	—	12
Total:	1,273,260	301,952	52,270	513,552	6,442	26,061
Nepal	1,843	—	189	—	—	—
Grand Total:	1,275,103	301,952	52,459	513,552	6,442	26,061

*The figures shown are the actual despatches by the 'Central Fertilizer Pool' during the respective years, irrespective of the year of allocation.

Source: [1] Ministry of Food & Agriculture, New Delhi
[2] Rallis India Ltd., Bombay
[3] New Central Jute Mills Co., Ltd., Varanasi

[FAI Inf. Serv., 7 (20) (1966), 9]

TABLE 12—CONSUMPTION OF FERTILIZERS PER UNIT AREA OF AGRICULTURAL LAND 1965-66

State	Consumption, lb/acre				Consumption, kg/hectare			
	N	P_2O_5	K_2O	Total	N	P_2O_5	K_2O	Total
Andhra Pradesh	4.93	1.92	0.17	7.02	5.53	2.15	0.19	7.87
Assam	1.39	0.66	0.10	2.15	1.56	0.74	0.11	2.41
Bihar	2.48	0.27	0.11	2.86	2.78	0.30	0.12	3.20
Gujarat	2.42	0.97	0.19	3.58	2.71	1.09	0.21	4.01
Jammu & Kashmir	2.83	0.11	—	2.94	3.17	0.12	—	3.29
Kerala	2.73	1.45	7.09	11.27	3.06	1.62	7.95	12.63
Madhya Pradesh	0.71	0.34	0.10	1.15	0.80	0.38	0.11	1.29
Madras	7.98	1.93	2.05	11.96	8.94	2.16	2.30	13.40
Maharashtra	2.35	0.62	0.51	3.48	2.63	0.69	0.57	3.89
Mysore	2.15	0.70	0.53	3.38	2.41	0.79	0.59	3.79
Orissa	1.74	0.12	0.11	1.97	1.95	0.14	0.12	2.21
Punjab	4.06	0.29	0.11	4.46	4.55	0.32	0.12	4.99
Rajasthan	0.48	0.06	0.05	0.59	0.54	0.07	0.06	0.67
Uttar Pradesh	3.43	0.20	0.19	3.82	3.85	0.22	0.21	4.28
West Bengal	4.13	0.95	1.08	6.16	4.63	1.07	1.21	6.91
Delhi	4.95	1.49	0.12	6.56	5.55	1.67	0.14	7.36
Himachal Pradesh	1.03	0.19	0.01	1.23	1.15	0.21	0.01	1.37
Manipur	2.61	0.93	—	3.54	2.93	1.04	—	3.97
Tripura	0.54	0.02	—	0.56	0.61	0.02	—	0.63
Nagaland	0.21	0.18	—	0.39	0.24	0.20	—	0.44
Pondicherry	11.02	1.34	—	12.36	12.35	1.50	—	13.85
Andamans & Nicobar	0.84	—	—	0.84	0.94	—	—	0.94
India:	2.94	0.67	0.46	4.07	3.30	0.75	0.51	4.56

Note: Agricultural land includes net area sown more than once, permanent pastures, other grazing lands and land under miscellaneous tree crops and groves.

[FAI Inf. Serv., 7 (1966), 22, 10]

TABLE 13—IMPORTS OF NITROGENOUS FERTILIZERS

(metric tonnes)

Articles and Country from which Imported	1965-66
*Ammonium Sulphate**	
Canada	38,052
Germany East	57,356
United Kingdom	29,137
U.S.A.	668,756
U.S.S.R.	99,604
West European countries	88,415
Total:	981,320
*Urea**	
Arabia	6,700
Colombia	4,300
Germany West	3,453
Holland	25,824
Iran	5,000
Italy	20,830
Japan	134,132
Rumania	3,000
West European countries	112,090
Total:	315,329
*Chilean Natural Nitrate of Soda***	
Chile	5,248
*Ammonium Chloride**	
Japan	26,500
U.S.A.	2,500
Total:	29,000
*Ammonium Sulphate Nitrate (26% N)**	
Germany West	25,553

Source: *Ministry of Food, Agriculture, C.D., & Cooperation, New Delhi.
**Rallis India Ltd., Bombay.

[FAI Inf. Serv., 8 (1) (1967) 8]

EDITOR'S REPORT FOR 1966

With the issue of Vol. 3 (1966) No. 4, TECHNOLOGY completes three years of existence. It has now developed into a full-fledged research journal, perhaps only of its kind in India covering all aspects of fertilizer and allied technologies. It is still issued free of charge; so it is sent as complimentary copies to the national laboratories and research institutes, scientific libraries, learned societies, scientific journals, related government departments, etc. However, we are happy to receive increasing numbers of enquiries from India and abroad for subscribing this quarterly and for reprints of papers appearing in it. We are now exchanging with about 42 scientific journals/bulletins/periodicals, some of which are well established, including a few foreign ones.

Papers and short communications appearing in TECHNOLOGY are now being abstracted by the Chemical Abstracts and Biological Abstracts of the USA, Analytical Abstracts, NPKS Abstracts, Soils & Fertilizers, Journal of the Society of Food & Agriculture and Journal of the Applied Chemistry of UK Chemisches Zentralblatt of Berlin, Referativnyii Zhurna of Moscow, the Indian Science Abstracts (INSDOC etc. Southeast Asia Abstracts of Manila (Philippines has also agreed to abstract it. Interest has been show by scientists working in some national laboratories t publish their papers in TECHNOLOGY; in fact, paper from them and other scientists are now welcome.

We make all efforts to get the papers thoroughly re fereed before publishing them. The time taken for re fereeing, however, varies widely, say from one to abou eight or nine months. We are extremely fortunate i getting valuable voluntary help from specialists an experts in India and abroad for refereeing the manus cripts for which our grateful thanks are due to them Thanks are also due to the members of the Publication Committee for TECHNOLOGY for co-operation an assistance. Lastly, our thanks are due to Messrs Easten Printers, Calcutta for printing this bulletin.

Possibility of CP Violation in Case of Anti-Deuteron

By

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It is shown that by studying the life-times of anti-nucleons in the decay of anti-deuteron and that of anti-deuteron itself in exactly the same environment, one can arrive at a clue which would enable us to conclude quite decisively either against or in favour of the concept of charge conjugation invariance.

Introduction

The existence of anti-deuteron* in nature has been established by the Columbia University physicists in June, 1965. Their conclusion is based on their observations "corresponding to real particles of negative charge and mass within ± 3 per cent of that of the deuteron". In their experiment they found that the rate of production of $\bar{d}$ relative to *Pions* was

$$\frac{d}{\pi}=(5.5\pm1.5)\times10^{-8}\ (5\ \mathrm{BeV/c}) \quad .. \quad (1)$$

Their conclusion is supported by their results in fitting high energy d^+ production without particle "pickup" processes. By making assumptions that if in the d production anti-nucleons are produced independently in 30—BeV collisions then 5—BeV $\bar{d}$ rate has been estimated as

$$\frac{\bar{d}}{\pi}=\left[\left(\frac{P_a n)}{Pn}\right)_{2.5\ \mathrm{BeV/c}}\right]^2\left(\frac{d^+}{\pi}\right)_{5\ \mathrm{BeV/c}}\Pi_i C_i \quad .. \quad (2)$$

where

$P_a n$ = probability of anti-nucleon production
Pn = probability of nucleon production
& C_1 = correction factor whose combined effect is less than $\frac{1}{10}$

* The present author also saw the possibility of existence of anti-nuclei for very light nuclei in nature more than a year before it was actually encountered by the Columbia University physicists. He, however, wrote to Professor Bernard T. Feld of the Massachusetts Institute of Technology about this at a time which by chance coincided with the announcement of the Columbia physicists.

The expression (2) has been finally deduced to

$$\frac{\bar{d}}{\Pi}=15\times10^{-8}\ \Pi_i C_i \quad .. \quad (3)$$

For $i>3$, however, expression (3) is nearly equal to expression (1), thus giving strong support to the mechanism of high energy d^+ production.

New Approach and Discussion

When the existence of anti-deuteron has already been established in nature, according to CPT invariance theorem bound state concept should be valid for it also. But as CP violation has already been suggested theoretically by the present author[1], and experimentally by V. L. FITCH[2] and others, and P. FRANZINI** etc., the study of the physical behaviour of anti-deuteron might provide us a further clue for testing this theorem. For this purpose, in the following arguments the fundamental assumption will be: *even if bound state concept is true for anti-deuteron we would treat the anti-nucleons to be existing more or less independently i.e. they would be practically in unbound state because the binding force between them would be negligibly small and that it would have very little overall contribution compared to the annihilation force between the anti-nucleons and the environmental material medium.* As we cannot by any means avoid this *annihilation force*

** Although Franzini's experiment has been challenged by CERN Physicists whose experiment apparently revives—CP invariance in electromagnetic interaction.

arising due to *annihilation bonds* between matter and anti-matter, we must consider this annihilation force in case of anti-matter in general.

Now deuteron, as we know about its existence in nature, is a stable combination. Among its two constituents proton is stable whereas neutron is unstable. Since we have not yet been able to discover any such stable combination in nature whose all the constituents are unstable, the cause of the deuteron stability may reasonably be attributed to stable proton and some kind of permanent binding force emanating from it to hold neutron permanently in its vicinity. Then according to symmetry principle—in the *so-called* anti-universe—anti-deuteron would be stable because of anti-proton stability there.

Now, let us consider the following:

(1) a number of different suitable material media may be chosen; in each of which let us produce and determine the life-times of anti-proton, anti-neutron, and anti-deuteron. Then, according to symmetry principle, the life-time of anti-proton should be equal to or greater than the life-time of anti-deuteron. If it is statistically not so, we should indirectly conclude against the concept of charge conjugation invariance.

(2) if the life-times of two anti-nucleons determined separately in exactly same environment differ, then in case of anti-deuteron (in the same medium) the annihilation process of the two anti-nucleons should not occur simultaneously, but there should be some time-lag between the two processes which if detected should confirm the bound state concept in case of anti-deuteron too. But if such time-lag is not detected because of its non-occurrence in the process and that anti-deuteron is annihilated as one physical entity in itself, we should abandon the bound state concept for anti-deuteron. And this should mean a deadly blow to mirror symmetry concept of Dirac. Thus, determined separately in the same medium if:

$t_a p$ = life-time of anti-proton
$t_a n$ = life-time of anti-neutron
$t_a d$ = life-time of anti-deuteron

then for

$$t_a p = t_a n = t_a d \qquad \text{.. (i)}$$

anti-deuteron should vanish without disintegrating into either of its constituents. But if

$$t_a p = t_a d < t_a n \qquad \text{.. (ii)}$$
$$\& \quad t_a n = t_a d < t_a p \qquad \text{.. (iii)}$$

then anti-deuteron should vanish by disintegrating itself either into anti-neutron as indicated in (ii) or into anti-proton as in case (iii)

For $t_a d > t_a p = t_a n$ .. (iv)

anti-deuteron would exist even after the life-time of anti-proton or that of anti-neutron indicating thereby that anti-deuteron should be governed by some hitherto unknown laws which should not be the case if symmetry principle is to be valid. That is to say, if CPT theorem is to be invariant then the life-time of anti-proton should not be less than that of anti-deuteron, of course all these life-times must be determined in exactly same environment. But if $t_a p < t_a d$ (statistically) we would have good reason to conclude against the concept of charge conjugation invariance.

Also, if $t_a p - t_a n = \Delta t$ say, then in the annihilation process of anti-deuteron both the anti-nucleons would not be annihilated simultaneously; on the other hand it is to be expected that anti-proton would be annihilated Δt time after the annihilation of anti-neutron. If this is so, then we would have reason to believe in the bound state concept for anti-deuteron too. But if it does not happen, we should conclude against the mirror symmetry concept.

We see the possibility of anti-deuteron having a single entity in itself formed when $\bar{\mathrm{o}}$ state due to proton mingles with $\bar{\mathrm{o}}$ state of neutron forming a single big 'hole' ($\bar{\mathrm{o}}$ state of deuteron) in the π-ocean just like two air bubbles of different size when mingled together in a liquid they form a single bigger air bubble. This mechanism might perhaps be able to explain the comparatively larger life-time of anti-deuteron (10^{-7} sec.) and its large absorption cross-section as determined by Lederman etc. in their experiment.

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The author expresses his deep sense of gratitude to Professor Bernard T. Feld of the Massachusetts Institute of Technology, for bringing in his notice the Lederman experiment in July, 1965, and for his comment "......but Science, if it to be exact and universally invarient must always insist on precise experimental verification of theories, irrespective of how simple and philosophically attractive they may appear, before we are willing to discard the tried and true in favour of the new." He is also grateful to Dr. K. R. Chakravorty and Dr. N. G. Basak of the Central Fuel Research Institute, Jealgora, for their constant encouragement. His than

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